# CHAPTER II

FUNDAMENTAL KNOWLEDGE AND LITERATURES SURVEY

2.1 Resorcinol – Formaldehyde gel (RF gel)

RF gel was firstly synthesized by Pekala and coworker in 1989. This prepare in sol – gel method which have resorcinol(R) and formaldehyde(F) as the precursors. Sodium carbonate is the most commonly used as alkaline catalyst and water is used as solvent. The mechanism is composed of two reactions are addition and polycondesation reaction which show in figure 2 [10].

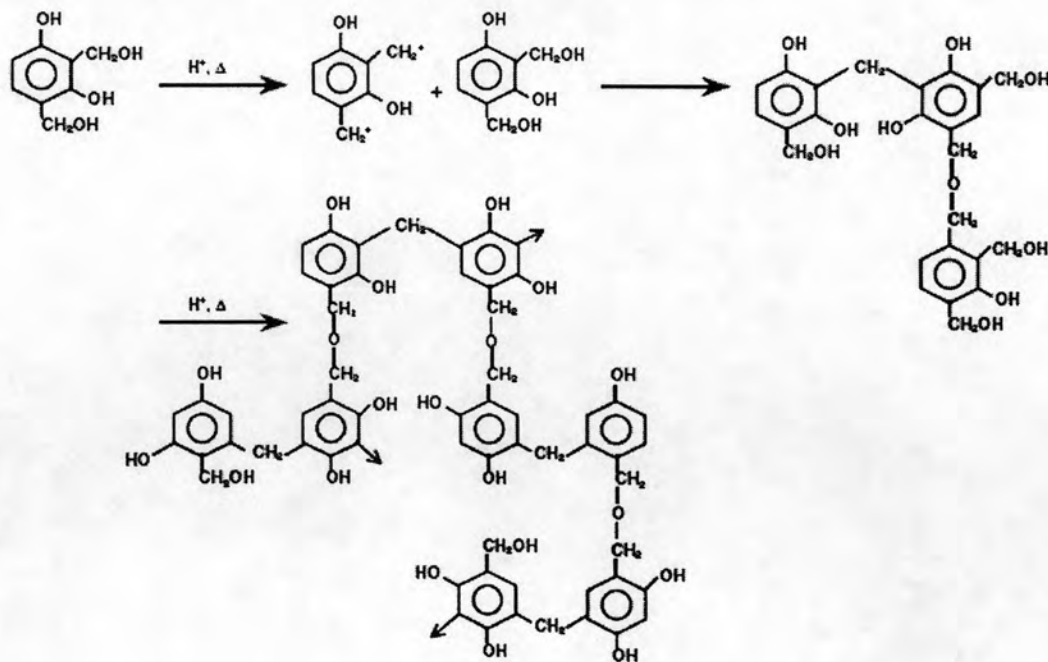**1. Addition Reaction**
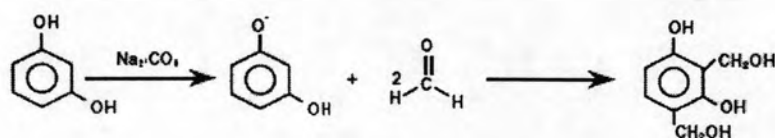
2. Condensation Reaction

Figure 2.1 The mechanism of Resorcinol – Formaldehyde gel synthesis [10]

The alkali catalyst is important for the formation of resorcinol anions during addition reaction. There resorcinol anions are more active than uncharged resorcinol. The products from additional reaction are the hydroxymethyl derivatives which are essential for the subsequent condensation reaction. This multi – steps mechanisms result in highly crosslinked clusters (7 – 10 nm diameters) of polymer. After completion of this step, the colloidal particles begin to aggregate and assembling a string of pearls that fills the original volume of the aqueous solution.
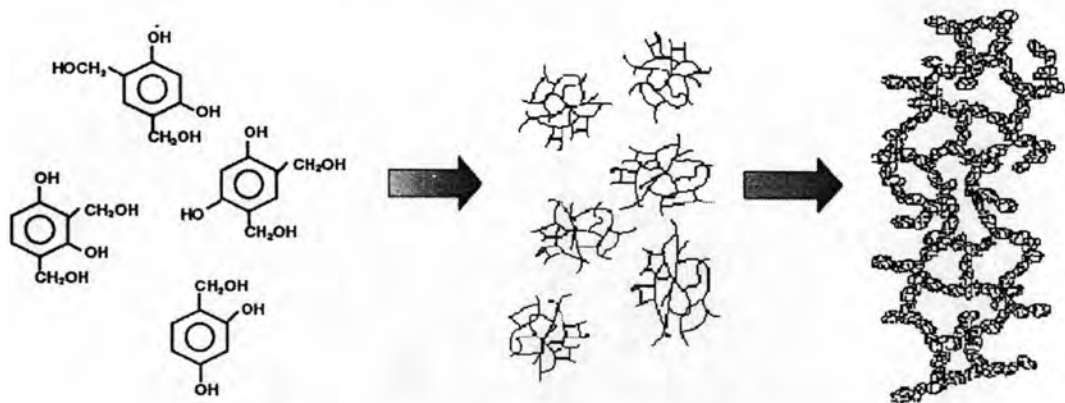

Figure 2.2 The growth of resorcinol – formaldehyde monomers [10]

2.2 Activation

The oxidizing agents most often used are steam, carbon dioxide, oxygen (air). During the activation of the carbonized product, first the disorganized carbon is removed, and the surface of the carbon crystallites becomes exposed to the action of the oxidizing agent. Details of the mechanism of this process, however, are not yet reliably understood.

The removal of unorganized carbon and the non-uniform burnout of elementary crystallites lead in the first phase of activation to the formation of new pores and the development of the microporous structure. In the subsequent phases, however, the effect that becomes increasingly significant is the widening of existing pores or the formation of larger size pores by the complete burnout of walls between

adjacent micropores. This leads to an increase in the volume of transitional and macropores, whereas the volume of micropores diminishes. As a measure of the degree of activation the so-called burn-off is usually used, which is the percentage weight decrease of the material during activation, compared to the original carbonized product. Sometimes the so-called activation yield is used, which is the weight of the resulting activated carbon expressed as a percentage of the carbonized intermediate product prior to activation. The burn-off (B) and the activation yield (A) are related thus:

$$B = 100- A$$

The carbon atoms, which form the structure of the carbonized product, differ markedly from one another in their affinity towards the activation agent. Those at the edges and corners of elementary crystallites, and those situated at defective places of the crystal lattice, are more reactive, because their valencies are incompletely saturated by interaction with neighboring carbon atoms. These places are the so called "active sites" on which reaction with the activation agent occurs; these sites represent only a small part, at the most only a few percent of the total surface exposed to the reaction. In the reaction of a gaseous activation agent with carbon, complex surface compounds are temporarily formed on the active sites, and on their decomposition the oxidized carbon is removed from the surface as gaseous oxides (carbon monoxide or dioxide). As a result of this, new incompletely saturated carbon atoms become exposed on the surface of the crystallites and the active sites are thus again prepared to react with further molecules of the activation agent. Details of the mechanism by which carbon reacts with steam and carbon dioxide are shown below.

2.2.1 Physical activation

Activation with steam

The reaction of steam with carbon is endothermic and a stoichiometric equation has the form:

$$C + H_2O \rightarrow H_2 + CO \qquad \Delta H = 117 \text{ kJ/mol}$$

The rate of gasification of carbon by a mixture of steam and hydrogen is given by the formula:

$$v = \frac{k_1 P_{H2O}}{1 + k_2 P_{H2O} + k_3 P_{H2}} \ldots \ldots (1)$$

where: P_{H2O} and P_{H2} are the partial pressures of steam and hydrogen, respectively, k_1, k_2, k_3 are the experimentally determined rate constants. The following reaction scheme is accepted as highly probable:

$$C + H_2O \leftrightarrow C(H_2O)$$
$$C(H_2O) \rightarrow H_2 + C(O)$$
$$C(O) \rightarrow CO$$
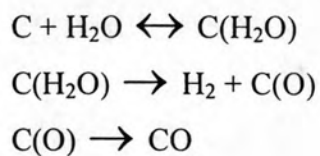
The inhibiting effect of hydrogen can be ascribed to its occupying active centers on which it becomes absorbed:

$$C + H_2 \leftrightarrow C(H_2)$$
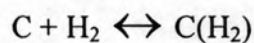
It was assumed that the first step of the reaction is the dissociated adsorption of water molecules according to the scheme:

$$2C + H_2O \rightarrow C(H) + C(OH)$$
$$C(H) + C(OH) \rightarrow C(H_2) + C(O)$$
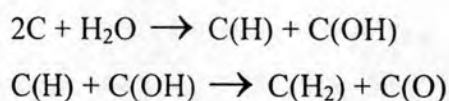
Hydrogen and oxygen are adsorbed at neighboring active sites, which account for about 2 percent of the surface area.

The reaction of steam with carbon is accompanied by the secondary reaction of water-gas formation, which is catalyzed by the carbon surface:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -42 \text{ kJ/mol}$$
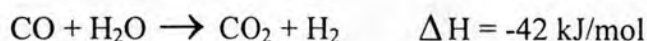
Activation with steam is carried out at temperatures from 750 to 950°C with the exclusion of oxygen, which at these temperatures aggressively attacks carbon and decreases the yield by surface burn-off. It is catalyzed by the oxides and carbonates of alkali metals, iron, copper and other metals; the activation catalysts usually employed in practice are carbonates of alkali metals, which are added in small amounts to the material to be activated.

Activation with Carbon Dioxide

For the rate of gasification of carbon by carbon dioxide an equation analogous to that for the reaction with steam has been derived:

$$v = \frac{k_1 P_{co2}}{1 + k_2 P_{co} + k_3 P_{co2}} \quad \ldots\ldots\ldots(2)$$

where: P_{co2} and P_{co} are the partial pressures, and k_1, k_2, k_3 are the experimentally determined rate constants. Although the quantitative validity of this equation has been subject to criticism, it is taken as a basis for consideration of the mechanism of the reaction of carbon dioxide with carbon.

The rate of this reaction is retarded not only by carbon monoxide, but also by the presence of hydrogen in the reaction mixture. When from the possible hypothetical schemes, which satisfy Equation 2, those are eliminated which include stages that have been experimentally shown to be improbable, two basic variants of the reaction mechanism remain:

Variant A

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

Variant B

$$C + CO_2 \rightarrow C(O) + CO$$
$$C(O) \rightarrow CO$$
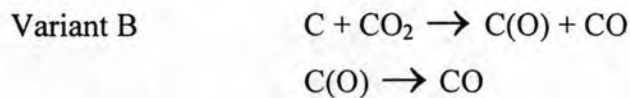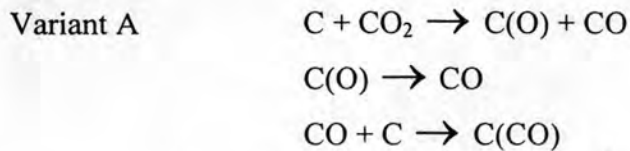
The basic difference between the two schemes lies in the explanation of the inhibiting effect of carbon monoxide. The rate of the reaction depends on the number of free active sites. In variant A, the rate of the reverse reaction is considered to be negligible and the inhibiting effect of carbon monoxide is supposed to be due to the blocking of active sites by their being covered by the adsorbed carbon monoxide. According to variant B the rate of the reverse reaction is considered to be significant, and the effect of carbon monoxide is explained as being due to a displacement of the reaction equilibrium in the latter equation.

Activation with carbon dioxide involves a less energetic reaction than that with steam and requires a higher temperature 850-1000 °C. The activation agent used in technical practice is flue gas to which a certain amount of steam is usually added, so that actually this is a case of combined activation. The catalysts for the reaction with carbon dioxide are carbonates of alkali metals [11].

There are many literature study about physical activation.

Yang T. (2003) [4]. They studied to prepare activation carbn from pistachio – nut shells by carbon dioxide activation in two step activation. The increasing in dwell time and activation temperature resulted in reduction of yield in activation carbon. For low activation temperature or short dwell time had the effect on release volatile more than the carbon burn off due to $C - CO_2$ reaction therefore the reduction in volatile content and increasing in fixed carbon. On the other hand, in case of higher activation temperature or longer dwell time had the effect on carbon burn off due to $C - CO_2$ reaction became more dominant which showed in the reduction of fixed carbon but increasing in volatile content. In pore evolution, with increased dwell time and activation temperature, continual devolatilization and $C - CO_2$ reaction occurred, resulting in the enhancement of exiting pores and the formation of new pores (microporosity range) which increased in BET surface area and micropore volume. However, too long a dwell time or too high a temperature would cause the widening of pores and the collapse of some pore walls. A low CO_2 flow rate was inadequate for the $C - CO_2$ reaction and the removal of releasing volatiles, resulting in reduced pore development in the activated carbon. Generally, CO_2 flow rates above the optimum value would not produce significant changes in the pore surface area.

Halat M. J. (2005) [5]. They studied to create molecular sieve properties from Polish high volatile bituminous coal with steam and carbon dioxide activation. 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 CO_2 activation developed micropore by opening (removing constrictions) and also widening the very narrow micropore. Steam activation leaded to greater micropore volume than CO_2 activation.

2.2.2 Catalysts in activation process

A number of inorganic salts and metals have exhibited catalytic activity in the gasification of different types of carbonaceous materials. Alkali metal salts, alkaline earth metal salts and transition metals have shown high activities in gasification. Alkali metal salts appear to have real potential in practical coal gasification.

Alkali metals catalysts

Alkali metal salts are the most active and widely used catalysts in gasification of carbonaceous material. They are known to disperse well on surface of carbon substrates, remain in molten state at reaction temperatures and are mobile during gasification. Gasification temperature can be lowered as much as $150 - 200\ ^{o}C$ in the present of 10 -20 percent of alkali metal carbonates and hydroxides. Alkali metal salts have been used to catalyze gasification of carbon, coke, char, and coals.

Alkali metal salts are also active in gasification of activation carbon with CO_2 and steam. Activation carbons have different physical and chemical properties when compare to graphite or pure carbon and therefore their gasification characteristics are expected to be different. Graphite is pure carbon and has low porosity whereas activated carbons contain carbon, hydrogen, heteroatoms and mineral matter with high porosity. In general, activation carbons are more active than graphite. The activity of catalysts in CO_2 gasification vary in the order of $Cs_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Li_2CO_3$ and activation energies vary in the reverse order of Li_2CO_3 (58.3 kcal/ mole) > Na_2CO_3 (52.4 kcal/mole) > K_2CO_3 (50.7 kcal/mole) > Rb_2CO_3 (47.9 kcal/ mole) > Cs_2CO_3 (46 kcal/mole). Steam gasification of activated carbons has also carried out with K_2CO_3 as catalyst. The conversions of activation carbons increase with time and K_2CO_3 loading at a temperature of $800\ ^{o}C$.

Mechanism of Alkali Metal Catalyzed Gasification

The mechanisms of catalyzed gasification depend upon type of catalyst, nature of carbon substrate and gasification medium.

K_2CO_3 and graphite have been used in most of the studies. The mechanisms show gasification catalysis takeing place due to the occurrence of several parallel and consecutive chemical reactions. The first logical step is chemisorptions of catalyst and gasification medium (CO_2 or steam) on surface of carbon substrate. The second step appears to be chemical interaction between catalyst and substrate which produces active species on the surface. The surface active species are probably mobile and act as active centers where gasification takes place. There is a lot of controversy about the type and nature of active species formed in the second step. The important species are metals, metal oxides, metal hydrides, hydroxides, complexes of metal-carbon (M-C), Metal-Oxygen (M-0) and Metal-Oxygen-Carbon (M-O-C) type and intercalates of Metal-Carbon (C_nK). The third step is an oxygen exchange process which takes place at gasification sites due to interaction of CO_2 or H_2O with active species formed from catalyst and substrate. It appears that catalysts transfer oxygen from the gasification medium to substrate. Oxygen exchange appears to be an important factor in determining gasification rate. This similarity between rates of oxygen exchange and gasification suggests that oxygen exchange is an essential precursory step in gasification and it takes place at gasification sites. Oxygen exchange rate is higher than gasification rate and therefore it does not control rate. The apparent activation energies of catalytic gasification suggest that rate is controlled by chemical reactions. The fourth step is the catalyst regeneration process which takes place either concurrent or subsequent to the third step by the interaction of gasification medium with surface active complexes.

Moreover, McKee et al.[22] proposed a kinetic scheme three elementary reaction for potassium in CO_2 activation

Carbothermic reduction

$$K_2CO_3 + 2C \longrightarrow 2K + 3CO$$

Oxidation

$$2K + CO_2 \longleftrightarrow K_2O + CO$$

· Carbonate formation

$$K_2O + CO_2 \longleftrightarrow K_2CO_3$$

Alkaline earth metals catalysts

Alkaline earth metal salts have also been used in the gasification of graphite, chars and coals. Alkaline earth metal carbonates have been used to catalyst steam and CO_2 gasification of graphite and their activities have been found to vary in the order of $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$. A number of barium salts have also been used in CO_2 and steam gasification of graphite and activities have been found to vary in the order of $BaCO_3 > Ba(NO_3)_2 > BaO > BaCl_2 > BaSO_4$. Several differences have been observed in the catalytic behavior of alkaline earth and alkali metal catalysts. Alkaline earth metal carbonates have been found to possess lower activities than alkali metal carbonates. The activities in CO_2 gasification of char have varied in the order of $K_2CO_3 > Na_2CO_3 > Li_2CO_3 > Cs_2CO_3 > BaCO_3 > SrCO_3 > CaCO_3$. $BaCl_2$ has been found to be an active catalyst but alkali metal chlorides are found to inhibit gasification of char. The activities of alkaline earth metal carbonates have been found to be independent of concentration in the range of 5-20 percent but activities of alkali metal carbonates increase with concentration until the surface of carbon substrate is saturated with catalyst sites [12].
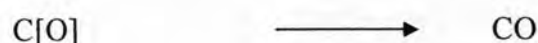
There are many mechanism of alkaline earth metal catalyzed gasification of carbon are proposed.

McKee proposed mechanism of alkaline earth carbonate in CO_2 gasification [12].

$$MCO_{3(s)} + C_{(s)} \longleftrightarrow 2CO_{(g)} + MO_{(s)}$$

$$MO_{(s)} + CO_{2(g)} \longleftrightarrow MCO_3$$
$$\text{where M = Ba, Sr, Ca, Mg}$$

Kapteijn proposed mechanism of calcium on steam gasification with graphite [22].

$$CaO + H_2O \longrightarrow CaO.O + H_2$$

$$CaO.O + C \longrightarrow CaO + C[O]$$

$$C[O] \longrightarrow CO$$

There are many literature study about using the alkali and alkaline earth for catalyst in activation process.

Cazorla – Amoros D. (1996) [21]. They studied the effect of calcium on porosity development during activation of a char from almond shell in steam and CO_2 activation. The char is immersed in calcium acetate solution (1.5 M), in the proportion of 10 ml solution/g char at 335 K for 24 h. For steam activation of the samples studied the effect of the catalyst is not very important, whereas the contrary happens for CO_2 gasification in this study. In fact, reaction rate with steam when the catalyst is present is only about 1.5 times higher than that for the uncatalyzed reaction. The CaO particles formed after heat treatment is more relevant to interpret the activation process. The CaO particle size distribution and the rates of sintering and gasification will determine porosity development. In case, a high ratio of carbon gasification to CaO sintering rates (the case of CO_2, activation) would cause an important development of porosity, causing an increase in pore size throughout a broad range of pores. The formation of pores in the range of mesoporosity and macroporosity is

explained by the movement of CaO particles due to carbon gasification and surface diffusion that experience CaO particles with size close or larger than 6 nm. In contrast, a small ratio of gasification to CaO sintering rates (the case of H_2O gasification) the porosity is less developed because the resultant prolonged sintering would have caused greater deactivation of the catalyst.

Hayashi J. (2000) [6]. They prepared activation carbon from impregnated lignin with chemical activated (K_2CO_3, Na_2CO_3, KOH, NaOH, $ZnCl_2$ and H_3PO_4) and carbonized in nitrogen atmosphere by various temperature in 500 – 900 °C ranges. The activation carbon were activated by $ZnCl_2$ and H_3PO_4 show 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 activation carbons were prepared by $ZnCl_2$ and H_3PO_4 activation increased in temperature over the range 500 – 600 °C, and decreased with an increased temperature in 600 – 900 °C from the result of carbon structure shrinks. They indicated that, $ZnCl_2$ and H_3PO_4 worked effective as activating reagents below 500 °C. They also proposed $ZnCl_2$ worked as dehydration reagent and restricted the formation of tar and promoted the charring of the carbon below 600 °C. Consequently, the carbon structure was modified and the surface area increased. 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 increased temperature up to 800 °C. The pores enlarge up to this temperature. Above 800 °C, the excess enlargement induces combination of pores, resulting in an increasing of mesopore and reduction of micropore volume. They propose that, K_2CO_3 modified 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 in activation below 500 °C. The temperature above 600 °C carbon was removed as CO and the surface area and the pore volume increased.

Okada K. (2003) [7]. They prepared activation carbon from old newspaper and paper prepared from simulated paper sludge by using the chemical and physical (steam) activation. 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). There were show little effect of different anions. They proposed 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. Their suggestion the smaller cations have little effect on the expansion of interlayers but the larger cations expanded interlayers causing 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. From the result, there were the differences in these microstructures were suggested to be caused by differences in the melting points and vapor pressures of the activating reagents. Moreover, in the case of HCl washing activation carbon show larger BET – surface area and pore volume than without washing sample. This represented the HCl washing was effective in reduce ash content.

Miyamoto J. (2005) [8]. They studied to produce mesoporosity in activated carbon fiber (ACF) which had uniform micropore and high surface area using chemical and physical activation. 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 mesopore and 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 there was no mesoporosity in K_2CO_3 since an insufficient activation

temperature 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 K2CO3 blocked the pore thus decreasing microporosity.

Lei S. (2006) [9] In their work activation carbon fibers (ACF) were impregnated with $Ca(NO_3)_2$ solution and activated by steam. 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 h. The increasing of $Ca(NO_3)_2$ 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 $Ca(NO_3)_2$ impregnation partially transformed micropores to mesopores. The pore size distribution of mesopores was very board considerably (20 ± 10 nm). Accordingly, the longer activation time (2 h) and temperature (800 – 900 $^\circ$C) resulted in an increasing mesopore volume.