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Preparation and structure characterization of carbons prepared from resorcinol-formaldehyde resin by CO_2 activation

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Abstract In this work, carbon xerogels with a high pore volume and surface area (up to $2.58\ \mathrm{cm^3/g}$ and $3200\ \mathrm{m^2/g}$ respectively) have been synthesized using the sol-gel polycondensation of resorcinol (R) with formaldehyde (F) in a basic medium of monoethanolamine (MEA), followed by drying and pyrolysis. This medium (MEA) has not been used in previous investigations. The effect of activation with CO_2 on the pore size distribution and the chemical functional groups has been investigated using N_2 (77 K) adsorption, FTIR and elemental analysis techniques. A series of experiments has been conducted to investigate the effect of activation time and activation temperature. Activation of the samples was carried out at 850, 900 and 980 °C for times ranging from one to three hours. Within the range of activation conditions, an increase in activation time at 850 °C results in a continuous steady rise of the BET surface area and total pore volume. However, at the two higher temperatures, the surface area shows a maximum when plotted against activation time. FT-IR results show that the use of MEA as a catalyst leads to the formation of nitrogen functional groups in the surface of the resin.

Keywords Activated carbon · Xerogels · CO_2 activation

1 Introduction

Activated carbons are sorbents with a highly developed porosity—especially in the micro and meso range—which are used in a wide range of applications, including gas-phase and liquid-phase adsorption processes (Sircar et al. 1996; Guo and Lua 2002b). Activated carbons can be produced from different precursors, including coals of different rank, and lignocellulosic materials, by physical or chemical activation processes (Guo and Lua 2003; Lua et al. 2006). In general, the principal properties of manufactured active carbons depend on the type and properties of the raw material used. Recently, increasing attention has been focused on using polymer precursors as a feedstock for activated carbons. Resorcinol–formaldehyde resins make excellent raw materials for the production of activated carbon with a highly-developed porosity and surface area because of the following reasons: the considerably high fixed-carbon content, high inherent purity, controllable macropore and micropore structure and relatively low price of the reagents (Tennison 1998; Hayashi et al. 2002; Yamamoto et al. 2002; Park and Jung 2002).

Most of the literature is based on the effect of the synthesis recipe of the resorcinol-formaldehyde aqueous solution on the structure of the resulting carbon. In addition, sodium carbonate was used as a common basification agent for the condensation reaction. However, there is little published work on how the activation conditions (activation time and temperature) impact on the development of the micro-, meso- and macro-porous structure, especially when monoethanolamine (MEA) is the catalyst.

In the synthesis of activated carbon by physical activation, when a particular precursor is used, it is mainly the activation process that determines the classification of the final material. So, it is instructive to conduct the activation under conditions that would yield an activated carbon with desirable textural and surface chemistry properties. From the survey, it was found that the effect of activation temperature on

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the porosity of the activated carbon varies with the raw material, and the experimental conditions cannot be extrapolated from one precursor material to another. Consider the case of activated carbon produced from a raw material of used tyres, and activated with a mixture of steam and carbon-dioxide. The BET surface area of the activated carbon increased with activation time reaching a maximum of 432 m^2/g after 120–150 min at a temperature of 970 °C and a burn-off level of 60–65 wt.% (Zabaniotou et al. 2004). Wigmans (1989) activated extruded peat semi-coke and showed that increasing the activation temperature from 860 to 1040 °C had no significant effect on the total pore volume. However, at temperatures above 900 °C, the macroporous volume decreased slightly with increasing burn-off. Guo and Lua (2002a) activated carbons prepared from oil-palm shell and showed that increasing the activation temperature from 773 to 1173 K leads to a progressive increase in the BET surface area; however the maximum surface area obtained was 1366 m^2/g. In another study on oil-palm shell, Daud et al. (2002) found that within the temperature range 800 to 900 °C, an increase in the activation temperatures had no significant effect on the mesopore and macropore development. In general, the activation process is usually carried out in presence of a suitable oxidizing agent such as steam, carbon-dioxide, air or oxygen. For steam and carbon dioxide activation, the temperature is generally in the region of 800 to 1000 °C, while steam activation starts in the temperature region of 700 to 750 °C. However, for oxygen activation, a lower temperature of 300 to 500 °C is usually employed to avoid combustion. The activation process, together with the intrinsic nature of the precursors, strongly determines the characteristics of the resulting activated carbons (Daud et al. 2002; Manocha 2003). According to the preceding discussion, this work is distinctive from previous work in a number of ways. First, it involves the development and modification of the resorcinol-formaldehyde sol-gel synthesis procedure by using a new basic medium to make a carbon xerogel with a high surface area, controlled pore structure and new surface chemistry. Second, it also includes a study of the effect of activation time and temperature on the porosity, chemical structure and carbon yield of the activated carbons. Third, nitrogen (77 K) adsorption is employed to verify the effect of the pore structure on the adsorption properties. The overall aim of this work is to obtain an appropriate activated carbon that would be suitable for the separation of carbon dioxide present at low concentrations in nitrogen.

2 Experimental

2.1 Resin synthesis

The synthesis procedure for the carbon xerogels was similar to that reported elsewhere (Lin and Ritter 2000). However, monoethanolamine (MEA), (research grade, Aldrich) was used as the catalyst. RF resin were synthesized by the polycondensation of resorcinol (R) (1,3-dihydroxybenzene $C_6H_4(OH)_2$) (reagent-grade 98%, Aldrich) and formaldehyde (F) (HCHO) (37% in water, stabilized by 10–15% wt. methanol, Aldrich) using an initial R:F molar ratio of 1:2. Deionised water (W) was used as the diluent. The mixture was then stirred for 15 minutes. The vials were sealed and gelation was performed at 85 °C in an oven for three days. The solvent was then removed from the pores of the gel slowly: first by evaporation at 60 °C for 2 hours, and then further by exposing to a vacuum at 120 °C for 12 hours. The RF resin was then placed in a ceramic boat located in a tubular oven, and pyrolysis was carried out at a temperature of 850 °C for three hours with an argon flow rate of 100 ml/min.

2.2 Activation process

The next stage was to activate the samples using carbon-dioxide and a flow rate of 100 ml/min. The activation temperature was varied between 850 and 980 °C with a heating rate of 30 °C/min and an activation time between one and three hours. An argon flow was used during the heating and cooling steps. The resulting activated carbon samples were labelled using the convention RFAC-a-b, where a and b denote the activation temperature and activation time, respectively. The functional groups in the resin, char and activated carbon were qualitatively analyzed by FTIR (Perkin Elmer).

2.3 Carbon characterization

The porous structure of each sample of activated carbon was determined by nitrogen adsorption/desorption at 77 K using a Micromeritics (ASAP 2000) apparatus. Each sample was first degassed at 110 °C for 12 hours under vacuum, and then the isotherm was measured in the relative pressure range from 0.01 to 0.99. The BET analysis was performed for relative pressures between 0.06 and 0.2. The total pore volume was calculated from the amount of vapour adsorbed at a relative pressure of 0.975. Following the IUPAC nomenclature, the pore sizes 2 nm and 50 nm were adopted as the micro–meso and meso–macro boundaries respectively. The Horvath–Kawazoe method was used to investigate the micropore size distribution. The micropore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.2. The mesopore volume was calculated by subtracting the amount adsorbed at a relative pressure of 0.2 from that adsorbed at a relative pressure of 0.99. The DFT and slit-shaped pore models were then used to determine the mesopore size distribution. Finally, the average pore diameter was calculated from $(2 \times V/A)$.

Table 1 Analysis of resorcinol-formaldehyde resin, char and activated counterparts

Nomenclature	Ultimate (wt% dry-ash-free basis)				Proximate (wt%)			
	C	H	N	O	Moisture	Volatile	Fixed carbon	Ash
RF-Resin	62.98	5.45	0.43	31.15	4.92	61.79	33.29	0
RF-Char	80.59	4.23	0.40	14.81	1.23	17.45	81.32	0
RFAC-850-1	85.53	3.99	0.40	10.08	0.17	13.21	86.62	0
RFAC-900-1	91.23	2.39	0.39	5.99	0.87	7.80	91.33	0
RFAC-980-1	92.12	1.98	0.41	5.49	0.73	3.40	95.87	0

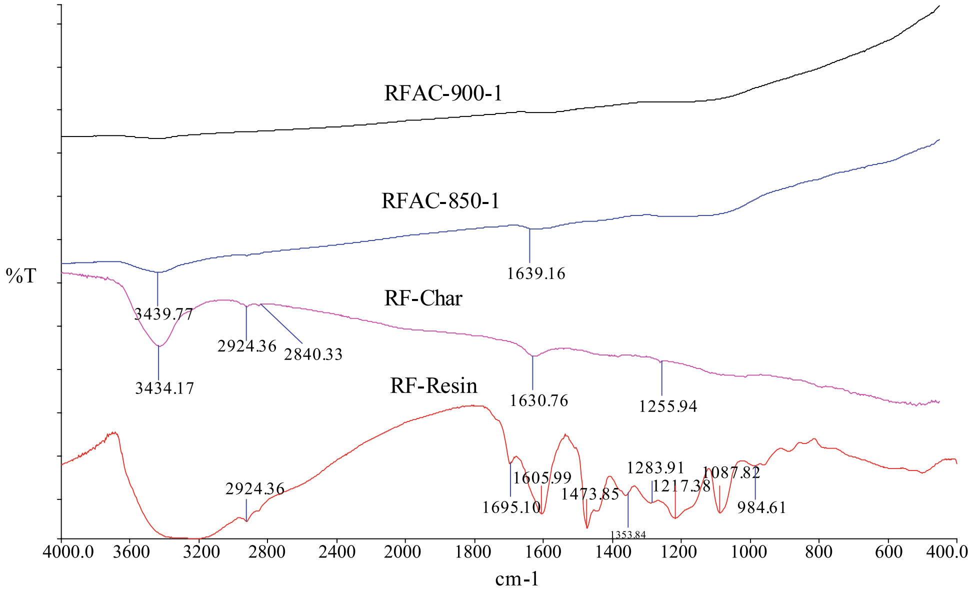


Fig. 1 FTIR spectra for the RF-resin, RF-char and for two activated carbons. For each activated carbon, the process was carried out with carbon-dioxide and an activation time of 1 hour: only the activation temperatures (900 and 850 °C) are different

3 Results and discussion

3.1 Ultimate and proximate analysis

The proximate and ultimate analyses of the resins and its activated counterparts were measured using a thermogravimetric analyzer (TGA; Perkin Elmer TGA 7) and elemental analyzer (Heraeus, CHN-O-RAPID), respectively. From Table 1, the nitrogen percentage in the resin structure indicates the development of nitrogen functional groups in the resin surface. This is due to the selection of MEA as the catalyst. Furthermore, it would appear that these groups are not affected by the activation process; this may be due the strong C–N bonds which are able to withstand extreme temperatures.

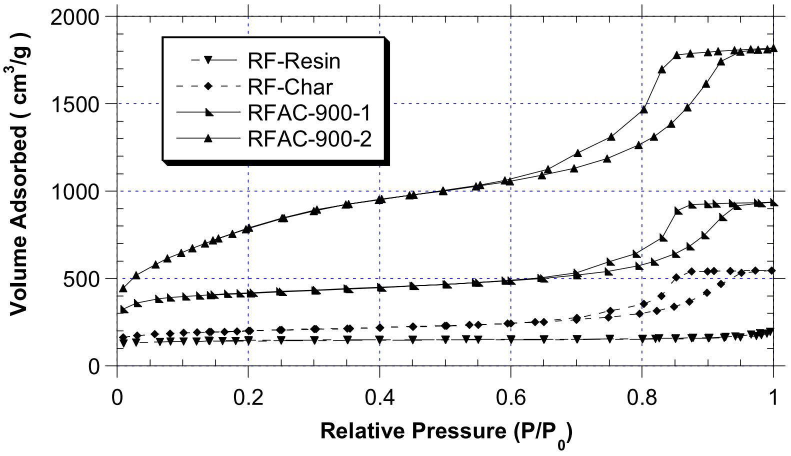
It is important to point out that the carbon percentage increased from 62.98% to 92.12% after the activation process. This could be attributed to this process causing the breaking of a significant proportion of the C–O and C–H bonds. Since the activation process is associated with weight loss, the volatile content must decrease significantly and this results in samples with significant fixed-carbon contents.

3.2 FTIR analysis

Figure 1 is a comparison of the IR spectra for the resin, char and for two activated samples: these correspond to the activation temperatures of 850 and 900 °C for a fixed activation time of one hour. The raw sample peak at 3570–3200 cm^{-1} is characteristic of the –OH group and can be linked to adsorbed water which decreases with increasing activation temperature. The other peaks cannot easily be assigned to specific groups. One might assume that the 1460–1480 cm^{-1} peak corresponds to the $-\mathrm{CH}_2-$ group, the 1600 cm^{-1} peak represents the aromatic group and the C–O–C group should be found between 1000 and 1300 cm^{-1} (several peaks appear in this interval). Among the several peaks in the region between 1000 and 1300 cm^{-1}, the peak at 1087 cm^{-1} represents stretching in the alkyl-phenyl ether (Costa et al. 1997; Coates 2000).

The main nitrogen functional groups incorporated in the resin structure due to the use of MEA as a catalyst are amides and amines, which correspond to the large band around 3430 cm^{-1}. The nitrile and lactame groups correspond to 2247 cm^{-1} and 1730 cm^{-1} respectively, and the amide group to 1625 cm^{-1} (Burg et al. 2002; Garcia et al.

Fig. 2 Nitrogen adsorption isotherms for the RF-resin, RF-char and for two activated carbons. For each activated carbon, the process was carried out with carbon-dioxide and an activation temperature of 900 °C: only the activation times (one and two hours) are different



2004). For the activated samples, the increase of activation temperature results in great variation of the peak intensities of all the described characteristic absorption bands together with peak shifting and/or peak merging. This is due to the transformation of the organic gel into a relatively pure carbon structure by the removal of any remaining oxide and hydrogen groups at these elevated temperatures.

3.3 Effect of activation time and temperature on the porous structure of the activated carbon xerogel

Figure 2 shows the nitrogen adsorption isotherm of the sample activated at 900 °C for activation times of one and two hours. For the sake of comparison, the isotherms of the resin and char are also presented. Comparison shows that the isotherms of the activated samples have much greater adsorbed volumes at lower relative pressures: this indicates that the activation process develops the microporosity in the char. The isotherms of the activated samples are a combination of type I and IV, which corresponds to a micro/mesoporous solid. The main feature of such an isotherm is the long plateau and a hysteresis loop at a higher relative pressure (Lowell 1991). However, by increasing the activation time, the isotherm shows a more open and rounder knee at a lower relative pressure and the slope of the plateau increases, indicating a broader pore-size distribution with larger micropores and an increasing mesoporosity. Furthermore, the nitrogen uptake increases significantly at a much higher relative pressure. It indicates that the meso/macropore structure in the sample is significantly developed with an increase of activation due to the widening of the micropores (Lin and Ritter 2000).

Figure 3 shows the mesopore size distribution for the sample before and after activation as calculated by the DFT using the slit-shaped pore model assumption. The estimated errors of the use of the model of slit-shaped pores are: 9% for RF-char, 3% RFAC-900-1 and 14% RFAC-900-2. It can be seen that the development of mesoporosity is strongly dependent on the activation process. For example, the sample before activation has one broad peak in the range of 30 nm while the activated forms have several peaks. Furthermore, as the activation time is increased, these peaks are shifted to smaller pore diameters indicating the formation of more mesopores. For an improved characterisation of the change in the microporous structure during activation, the micropore size distribution was calculated by the Horvath-Kawazoe method. Figure 4 shows the micropore size distribution as a function of activation time. It can be observed that all samples have *one* main peak which is centered around 1 nm (without any additional peaks) and as the activation time is increased, the micropore volume also significantly increased and the pore size distribution becomes wider. As stated above, it is found that activation results in enhancement of the micropore volume and micropore size distribution.

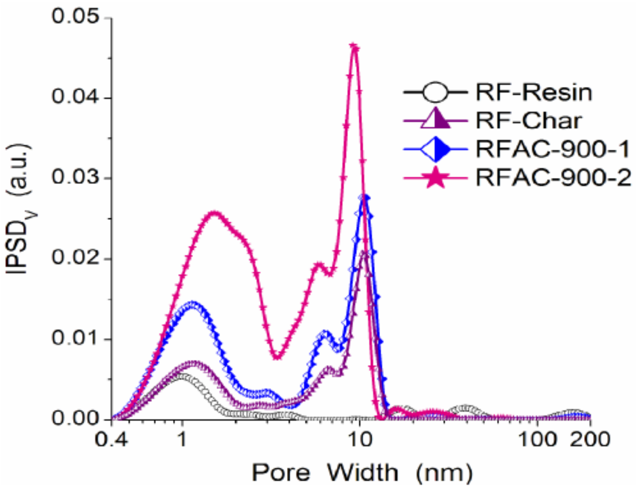


Fig. 3 Mesopore size distributions for the RF-resin, RF-char and for two activated carbons. For each activated carbon, the process was carried out with carbon-dioxide and an activation temperature of 900 °C: only the activation times (one and two hours) are different

Fig. 4 Micropore size distributions for the RF-resin, RF-char and for two activated carbons. For each activated carbon, the process was carried out with carbon-dioxide and an activation temperature of 900 °C: only the activation times (one and two hours) are different

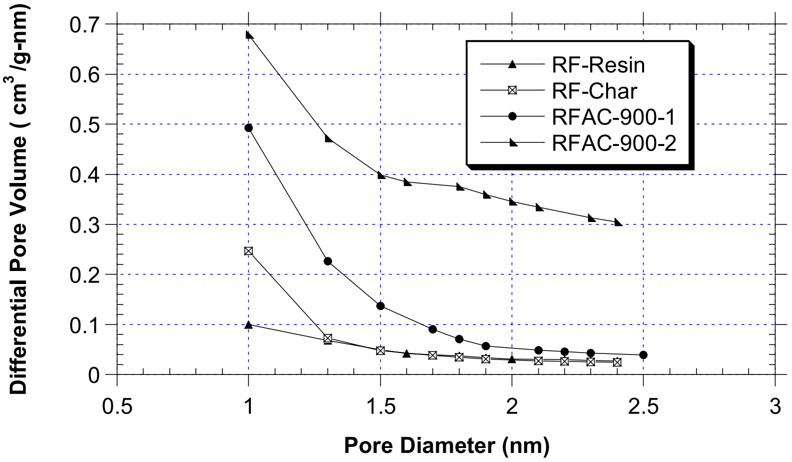


Fig. 5 Variation of the total pore volume with activation time for a fixed activation temperature of 900 °C

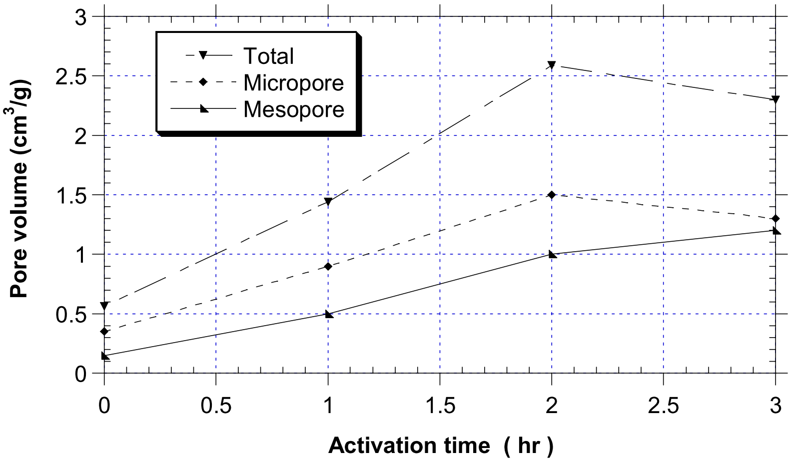
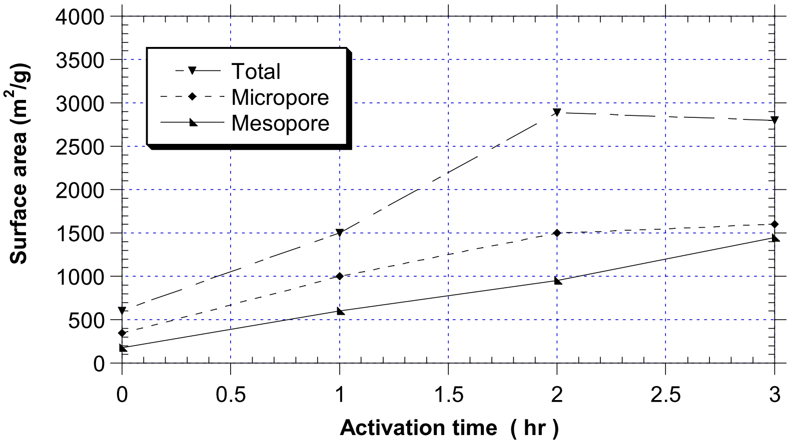


Fig. 6 Variation of the BET surface area with activation time for a fixed activation temperature of 900 °C



Figures 5 and 6 show the variation of the volume (total, micropore and mesopore) and surface area for a series of samples activated with carbon dioxide at 900 °C for various activation times. The total pore volume and surface area of the activated samples is mainly due to the micropores. This predominant microporosity is desirable for applications in the gas phase, including the removal of gaseous pollutants by adsorption. However, it should be noted that increasing the activation time at this temperature results in a continuous steady rise of the mesopores area and volume, while the micropore/total pore area and volume show a maximum and then decline with increasing time. This phenomenon could be attributed to the fact that during carbonisation the free interstices present in the carbon become filled

Fig. 7 Variation of the total pore volume with activation time for three different activation temperatures (850, 900 and 980 °C)

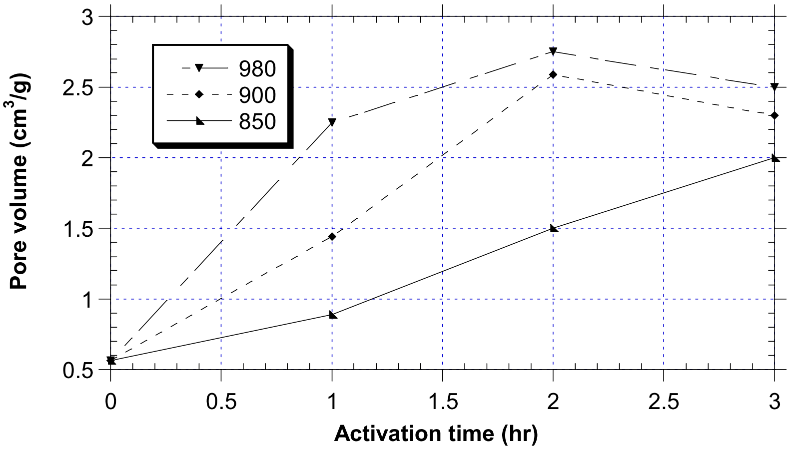
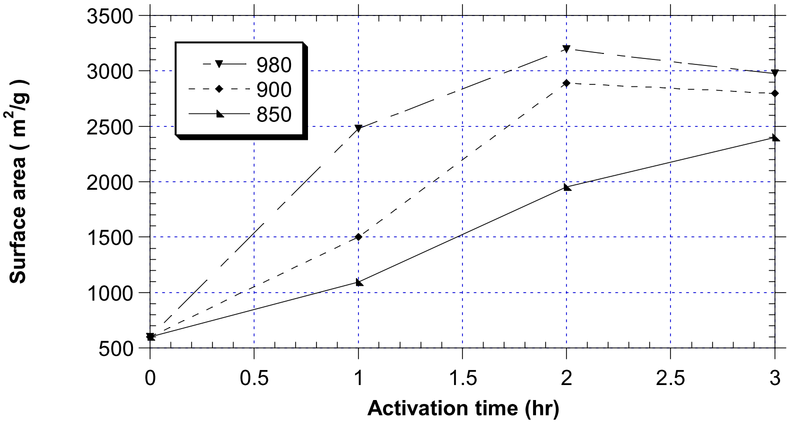


Fig. 8 Variation of the BET surface area with activation time for three different activation temperatures (850, 900 and 980 °C)



or at least partially blocked by disorganised carbon as a result of the deposition of tarry substances. At lower activation condition, development of the microporosity is mainly due to opening of the inaccessible pores blocked by tarry products. Any further increase in the micropore volume could be due to a pore-creating mechanism that occurs through selective activation, and the sequential burning of a carbon crystal: the first crystals to be burned are the single layer crystals, followed by disordered crystals and finally parallel group crystals. In the latter phase, excessive reactions lead to a "knocking down" of the pore walls by the activating agent, and this result in an increase in the number of mesopores and macropores. The volume of the micropores decreases and there is no significant increase in adsorption capacity or internal surface area (Manocha 2002). Another possible reason for the reduction in micropore volume is that as the extent of activation progresses, most of the sites tend to be at the exterior of the surface that this causes the particle to shrink: in this case, activation leads to an increase in pore widening (Guo and Lua 2002a; Leboda et al. 2003).

A series of samples was activated at temperatures of 850, 900 and 980 °C for activation times between one and three hours. Figures 7 and 8 show how the total pore volume and surface area, respectively, vary with the different activation conditions. The BET surface area and pore volume increased steadily with activation temperature: this was attributed to the strong dependency of the carbon–CO_2 reaction on the reaction temperature. For a fixed activation time, both pore volume and surface area increase with activation temperature. For a fixed activation temperature, however, the surface area and pore volume do not increase steadily with activation time. The activation time corresponding to the maximum surface area and pore volume shifts to a lower value as the activation temperature is increased. For example, for the activation temperatures of 900 and 980 °C, the surface area and pore volume decrease as the activation time is increased to more than 2.5 hours; while for the activation temperature of 850 °C, time corresponding to the maximum in surface area and pore volume is much greater than three hours.

To investigate the effect of the activation process on the activated carbon yield, the following (1) was used:

$$\text{Carbon yield (in wt \%)} = [W_1/W_2] \times 100, \qquad (1)$$

where W_1 and W_2 are the weights of the activated carbons product and the parent chars, respectively. Table 2 lists the

Table 2 Yield (%) of (solid) activated carbon for different activation conditions

Temperature	1 h	2 h	3 h
850 °C	78	57	42
900 °C	63	40	17
980 °C	38	21	5

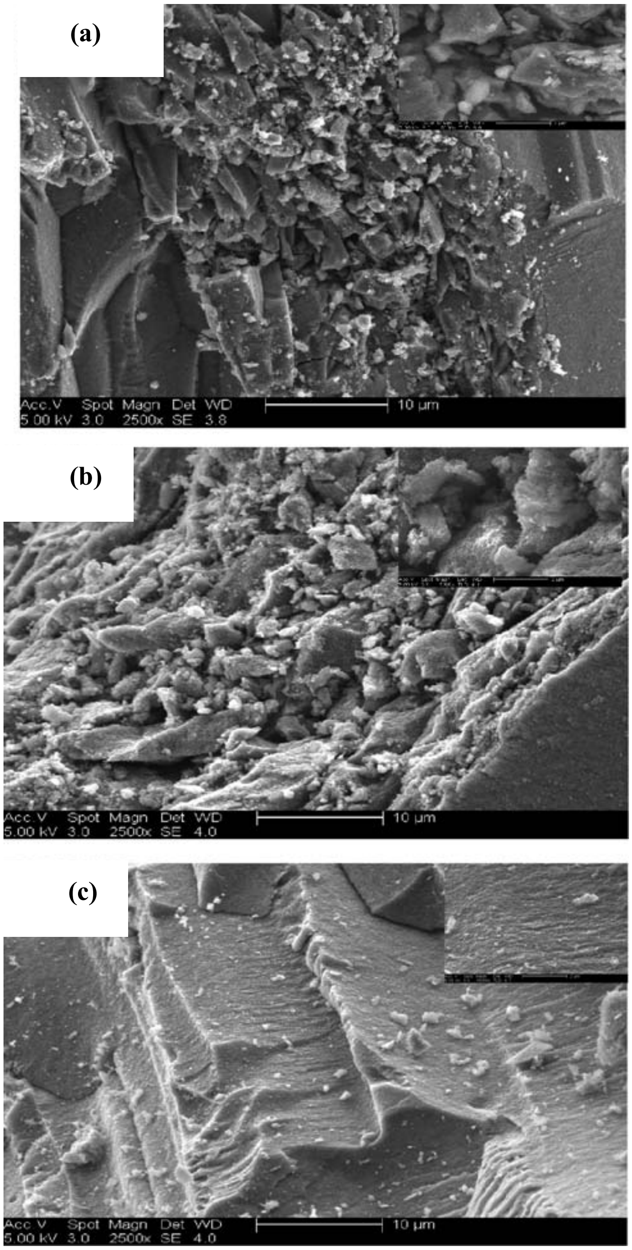


Fig. 9 SEM images of (**a**) parent resorcinol–formaldehyde (RF) resin, (**b**) RF-char and (**c**) activated carbon (activation conditions of 900 °C and 1 hr). The impeded images magnification is 5000×

solid yield of the samples activated under different conditions (time and temperature). As expected, the solid yields decreases with increasing activation time and temperature. Consider the activation time of one hour: the solid yield reduces from 78% to 31% as the activation temperature is increased from 850 °C to 980 °C.

3.4 Particle morphology characterization with scanning electron microscopy analysis

Figures 9a, 9b, 9c show the SEM images of the parent resin, char and activated sample (conditions of 900$^{\mathrm{o}}$C and one hour). For each material, there are two different scale images. There are few differences between the particle morphology before and after pyrolysis, despite a mass loss 40 to 50%. The SEM suggests that both the parent resin and char are made of interconnected particles with irregular shapes (aggregated particles without a clear boundary). The aggregated particles are interlinked to form a 3D network with a number of mesopores. Moreover, the extent of interlinking increases after pyrolysis and this is accompanied by an increase in the size of the mesovoids. Pictures taken at a higher magnification enabled measurement of an approximate particle diameter. For example, the diameter increases during pyrolysis from 3.5 μm (polymer) to 6 μm (carbon particles).

Figure 9c shows the SEM image for the sample activated at 900 °C for one hour. The sample has a compact structure. The high magnification image shows a particle surface with a large numbers of small pits distributed over the surface, indicating that most pore development occurs inside the particles.

4 Conclusion

In this work, it has been confirmed that resorcinol-formaldehyde synthesised with amine as a catalyst can be successfully converted to activated carbon with a high pore volume and surface area (up to 2.58 cm^3/g and 3200 m^2/g) and a carbon yield of 40%. For the lowest activation temperature employed (850 °C), both the pore volume and surface area increase with activation time. However, at the two higher temperatures (900 and 980 °C), the plots of pore volume and surface area with time show maxima. The initial increase in surface area/pore volume is probably due to opening of channels and the formation of micropores, while the decrease in surface area is probably due to the enlargement of micropores and removal of the pore walls. The carbon yield analysis shows that as the activation temperature is increased from 850 to 980 °C, the significant reduction in sample weight is due to a combination of the following factors: release of volatile matters in the carbonisation process, carbon burn-off and partial oxidation by carbon dioxide. These findings were confirmed by the results of the proximate analysis. The overall objective of this work is to demonstrate that there are a number of advantages and opportunities associated with producing activated carbons from resorcinol-formaldehyde resin with amine catalysis. The high inherent purity combined with the nitrogen functional groups on the surface and a controllable mesopore and micropore structure suggest many potential applications in the field of adsorption and catalyst support.

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