

Preparation of Activated Carbons from Bituminous Coals with Zinc Chloride Activation

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Activated carbons were prepared by chemical activation from two Australian bituminous coals in this study. The preparation process consisted of zinc chloride impregnation followed by carbonization in nitrogen. The carbonization temperature ranges from 400 to 700 °C. Experimental results reveal that an acid-washing process following the carbonization with ZnCl_2 is necessary for preparing high-porosity carbons. Surface area, pore volume, and average pore diameter of the resulting carbons increase with the carbonization temperature to a maximum at 500 °C and then begin to decrease. The maximum values of surface area and pore volume are larger for the carbon prepared from the coal with a lower O/C atomic ratio, while earlier findings from physical activation with CO_2 have shown an opposite trend. An increase in particle size of the coal precursor leads to a reduction in porosity of the resulting carbons. The duration of the carbonization period affects the porosity of the resulting carbons, and the influence varies with the activation temperature.

Introduction

Separation and purification of gas or liquid mixtures by adsorption has become a major unit operation in the chemical and petrochemical industries (Sircar et al., 1996). Activated carbons produced from various types of carbonaceous material have played a major role in this development. Because of its availability and cheapness, coal is the most commonly used precursor for activated carbon production (Ahmadpour and Do, 1996; Muñoz-Guillena et al., 1992; Bansal et al., 1988). Among coal-based carbons, bituminous products are in greater demand since they have greater density, hardness, and abrasion resistance and are more durable (Greenbank and Spotts, 1993). In the present study, Australian bituminous coals were chosen as precursors of activated carbon.

Pore structure, in terms of surface area and pore volume, is an important property of porous solids such as activated carbon. In general, activated carbons with both a high surface area and porosity, allowing large amounts of adsorption, are desirable. Practically, the type of porosity is dictated by the type of raw material employed; however, the method of activation is another parameter which may influence the final pore size distribution (Laine and Yunes, 1992). Basically, there are two different processes for the preparation of activated carbon: physical and chemical activation. Physical activation consists of carbonization of the raw material followed by gasification of the resulting char (Bansal et al., 1988; Wigmans, 1989). The other method, chemical activation, consists of carbonization at a relatively low temperature (e.g., 400–700 °C) with the addition of a dehydrating agent (e.g., ZnCl_2 , KOH, and H_3PO_4). These chemical reagents may promote the formation of cross-links, leading to the formation of a rigid matrix, less prone to volatile loss and volume

contraction upon heating to high temperatures (Illán-Gómez et al., 1996).

In our previous studies (Teng et al., 1996, 1997), preparation of activated carbons from Australian bituminous coals through physical activation (CO_2 gasification) has been extensively studied. Because of the low reaction rate between the activating agent and the char, a high temperature (>800 °C) for both carbonization and gasification was necessary. The development of the porous structure in the char was achieved by elimination of a large amount of internal carbon mass. The results have shown that activated carbons with high surface area can be obtained only at high extents of char burn-off. Therefore, the product yield is low for the preparation of activated carbons from the bituminous coals through physical activation.

In comparison with physical activation, there are two important advantages of chemical activation. One is the lower temperature in which the process is accomplished. The other is that the global yield of the chemical activation tends to be greater since char burn-off is not required. Among the numerous dehydrating agents, zinc chloride in particular is the widely used chemical agent in the preparation of activated carbon (Ahmadpour and Do, 1996; Caturla et al., 1991). However, the behaviors during preparation and the properties of the activated carbons from zinc chloride activation have not been thoroughly compared with those from physical activation. Since bituminous coals are used in the present study, the caking properties, which can be affected by the O/C atomic ratio in the raw coal, may play a role in determining the pore structure of the carbon prepared from chemical activation (Teng et al., 1996; Wigmans, 1989; Alvarez et al., 1994).

Within the above scope this study is devoted to the effects of different parameters on the preparation of activated carbon from bituminous coals with ZnCl_2 activation. These results, including coal type effects, behaviors during carbonization, and surface structures of the resulting activated carbon, are then compared

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Table 1. Coal Analysis (wt %)

	Black Water (BW)	Mt. Thorley (MT)
	Ultimate	
carbon	83.2	78.9
nitrogen	3.7	3.3
hydrogen	5.1	5.4
oxygen	7.4	11.8
sulfur	0.6	0.6
O/C atomic ratio	0.067	0.11
	Proximate	
moisture	2.7	3.1
volatile matters	26.7	33.1
fixed carbon	61.8	55.0
ash	8.9	8.8

with those obtained by CO₂ activation of the same source of raw material.

Experimental Section

Two Australian bituminous coals, Black Water (BW) and Mt. Thorley (MT), were used as the starting material. The proximate and ultimate analyses of the raw coals are shown in Table 1. The as-received coals were ground and sieved to two different particle sizes, 210–300 and 420–1000 μm , before being treated.

The analyses shown in Table 1 reveal that the bituminous coals have similar ash contents. The major difference in the ultimate analysis is the oxygen content, or the O/C atomic ratio, which represents a normalized property of each coal. The MT coal has a higher O/C atomic ratio than the BW. The O/C ratio has a great impact on the properties of the coals; e.g., in the proximate analysis the volatile matter increases and the fixed carbon decreases with the oxygen content of the coals. It has also been reported that, in the preparation of activated carbons from these coals with CO₂ activation, the reactivity in CO₂, the surface area, and the pore volume of the resulting carbons are all increasing functions of the O/C ratio of the coal precursors (Teng et al., 1996).

Chemical activation was performed with ZnCl₂. The experimental procedure used in the activation process was as follows: 20 g of coal was mixed, by stirring, with 100 g of an aqueous solution that contained 40 g of ZnCl₂. The chemical ratio, activating agent/coal, was 200% in this case. The mixing was performed at 85 °C for 3 h. After mixing, the coal slurry was subjected to vacuum drying at 100 °C for 24 h. The resulting chemical-loaded samples were then carbonized in a horizontal cylindrical furnace (25 mm i.d.) in an N₂ atmosphere, with a flow of 100 mL/min. The samples were heated at 30 °C/min from room temperature to carbonization temperatures in the range of 400–700 °C and then held at that temperature for different lengths of carbonization time (0, 1, or 2 h) before cooling under N₂. After cooling the carbonized products were washed sequentially with 0.5 N HCl (100 mL/g of char) and 85 °C hot water (150 mL/g of char) and then dried by vacuum at 50 °C.

In order to be clear about the carbonization process, a thermogravimetric analyzer (TGA; DuPont TGA 51) was employed to monitor the volatile evolution behavior, also in an N₂ atmosphere. A sample of 30–50 mg was used for each TGA analysis. It was found that the chemical and surface properties of the carbon obtained from carbonization in TGA were similar to those of the carbon prepared from the cylindrical furnace, although

the sizes of the samples carbonized in these two systems were different.

Specific surface areas and porosities of the samples were determined by gas adsorption. An automated adsorption apparatus (Micromeritics, ASAP 2000) was employed for these measurements. Adsorption of N₂, as a probe species, was performed at –196 °C. Before any such analysis the sample was degassed at 300 °C in a vacuum at about 10^{–3} Torr. Surface areas and micropore volumes of the samples were determined from the application of the BET and Dubinin–Radushkevich (D–R) equations, respectively, to the adsorption isotherms at relative pressures between 0.06 and 0.2. The amount of N₂ adsorbed at pressures near unity corresponds to the total amount adsorbed at both micropores and mesopores; and, consequently, the subtraction of the micropore volume (from the D–R equation) from the total amount (determined at $p/p_0 = 0.98$ in this case) will provide the volume of the mesopore (Rodríguez-Reinoso et al., 1995). The average pore diameter can be determined according to the surface area and total pore volume (the sum of the micropore and mesopore volumes), if the pores are assumed to be parallel and cylindrical.

A Hitachi S-4000 scanning electron microscope was used to study the structural features of the carbon surface.

Results and Discussion

Preparation of activated carbon by chemical activation principally consists of two consecutive steps: impregnation and carbonization. In the present study the effects of carbonization conditions on the properties of the resulting activated carbon were extensively examined. The influence of impregnation condition, however, was not the major concern. The activated carbons produced from chemical activation were also compared to those from physical activation (Teng et al., 1996). It should be noted that except for studying the influence of particle size, coal precursors with a size of 210–300 μm were used to produce carbons from different preparation conditions. The results are discussed separately as follows.

Carbonization Behavior. As stated in the previous section, carbonization has been implemented under an N₂ environment. The behaviors of volatile evolution during carbonization of the ZnCl₂-treated samples were monitored in TGA, and the results were compared to those of untreated coals. These samples were heated from 30 to 700 °C at a heating rate of 30 °C/min. Figure 1 shows the comparison of the carbonization behaviors of the BW samples. The results for the MT samples are similar to those shown in Figure 1. One can observe from Figure 1a that the carbonization process for the untreated sample can be approximately described by moisture and volatile lumps. Tar is probably a predominant product of devolatilization for a significant part of the process, so that a sharp peak for volatile evolution is observed. However, as shown in Figure 1b, the carbonization of the ZnCl₂-treated sample shows a different volatile evolution behavior. The weight loss is high, more than 60% during the heating stage up to 700 °C. Since the ZnCl₂-treated sample had a chemical ratio of 200%, evolution of ZnCl₂ must have been involved in the weight loss process.

In order to have a better understanding, a blank test was carried out to estimate the amount of ZnCl₂ evolved

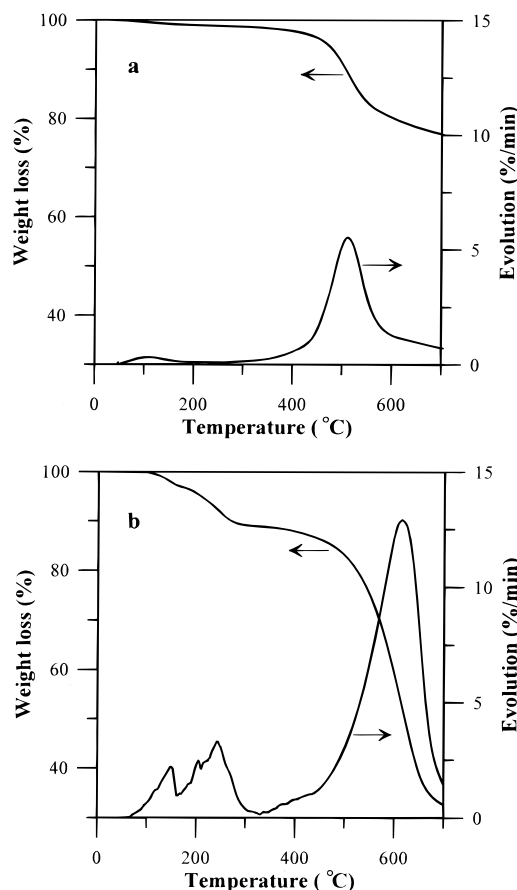


Figure 1. Weight loss and evolution rate during carbonization of the different BW samples: (a) untreated BW coal and (b) ZnCl_2 treated BW coal (wt % on an as-received basis; heating rate, 30 $^{\circ}\text{C}/\text{min}$).

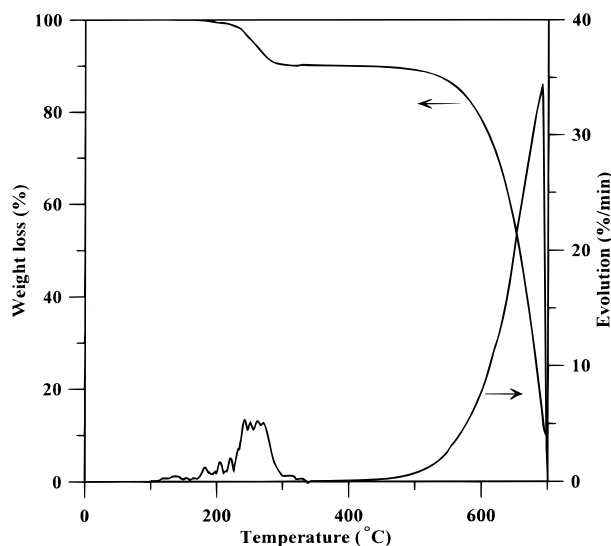


Figure 2. Weight loss and evolution rate during heating of the ZnCl_2 sample prepared from vacuum drying of an aqueous solution of 40% ZnCl_2 at 100 $^{\circ}\text{C}$ for 24 h (wt % on an as-received basis; heating rate, 30 $^{\circ}\text{C}/\text{min}$).

during the heating stage. In the blank test, a ZnCl_2 sample, prepared from vacuum drying of an aqueous solution of 40% ZnCl_2 at 100 $^{\circ}\text{C}$ for 24 h, was subjected to a similar analysis in TGA. The results of the blank test are shown in Figure 2. It can be observed that there are two distinct evolution lumps showing up during the heating: a smaller evolution occurs between

200 and 300 $^{\circ}\text{C}$ and a larger one at higher temperatures. One should notice that ZnCl_2 has a melting point of 283 $^{\circ}\text{C}$ and a boiling point of 732 $^{\circ}\text{C}$. The evolution at lower temperatures should be attributed to the release of moisture which is strongly associated with the solid-phase ZnCl_2 and becomes free as the ZnCl_2 becomes liquefied. At higher temperatures the evolution obviously represents the gradual evaporation of the liquid-phase ZnCl_2 . The results of this blank test confirm the earlier findings that activating reagent recovery goes down with increasing temperatures as a result of ZnCl_2 evaporation (Ruiz Beviá et al., 1984; Ahmadpour and Do, 1996).

By quantitatively comparing the evolution results of the ZnCl_2 -treated sample, which has a chemical ratio of 200%, with those from the blank test, it can be found that the release of moisture and ZnCl_2 represents most of the evolution from the ZnCl_2 -treated sample, indicating that ZnCl_2 plays an important role in retarding tar escape during carbonization (Illán-Gómez et al., 1996). As a matter of fact, the yield of activated carbon prepared from this chemical activation process is high, as compared with that from physical activation (Teng et al., 1996). For example, the yield, based on the chemical-free coal precursor, is close to 100% for preparing the BW carbon from 1 h of carbonization at 500 $^{\circ}\text{C}$ and around 80% from carbonization at 700 $^{\circ}\text{C}$. For preparing the MT carbon, the yield is around 86% from 1 h of carbonization at 500 $^{\circ}\text{C}$.

Effect of the Washing Process after Carbonization. After carbonization with chemicals the products are normally subjected to washing with acid and water (Caturla et al., 1991; Ahmadpour and Do, 1996). Washing with acid removes all the alkali and alkaline earth metals, and washing with water removes all basic and water soluble components in the carbon (Ahmadpour and Do, 1996). It is known that removing the chemicals left in the carbonized sample by washing will yield porosity in the carbon structure. In the present study, as stated in the Experimental Section, chars produced from carbonization with ZnCl_2 were subjected to acid washing, which consisted of sequential washings with 0.5 N HCl and 85 $^{\circ}\text{C}$ hot water. To test the effect of HCl washing, chars from carbonization at 500 $^{\circ}\text{C}$ for 1 and 2 h were subjected to a water-washing process, in which the carbonized products were washed sequentially with room temperature water (100 mL/g of char) and 85 $^{\circ}\text{C}$ hot water (150 mL/g of char).

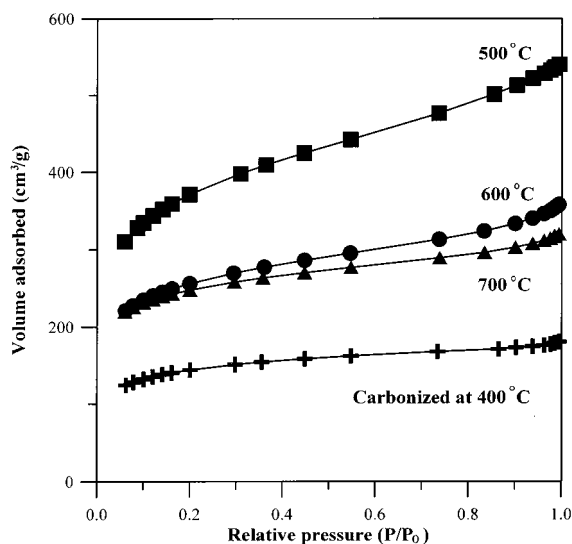
Surface structures of the carbons from different washing processes were measured, and the data obtained are shown in Table 2. Those of the unwashed carbons (carbonized samples with no washing treatment) are also presented in Table 2. The results presented in Table 2 clearly show that the porosity created in the carbon samples is mostly occupied by the chemicals in the structure. Low surface areas of the carbons with no washing treatment are because of ZnCl_2 left in the carbon, blocking pore entrances to the nitrogen molecules (Ahmadpour and Do, 1996). One should also notice that the micropore fraction of the total pore volume increases after washing, indicating that the blocking by chemicals mainly occurs on micropore entrances.

In a comparison of the results from the water-washing and the acid-washing processes, the total pore volume was higher for the carbons treated with acid washing than those with water washing. However, the

Table 2. Surface Properties of the Chars Treated with Different Washing Processes^a

carboni- zation time (h)	washing process	BET SA (m ² /g)	pore volume (cm ³ /g)	pore size distribution	
				micro (%)	meso (%)
BW Carbon					
1	no washing	91	0.112	38	62
1	water washing	887	0.479	87	13
1	acid washing	1300	0.828	75	25
2	no washing	210	0.155	65	35
2	water washing	668	0.360	88	12
2	acid washing	1180	0.693	81	19
MT Carbon					
1	no washing	116	0.091	60	40
1	water washing	894	0.476	89	11
1	acid washing	1080	0.649	79	21
2	no washing	123	0.088	67	33
2	water washing	727	0.394	87	13
2	acid washing	971	0.564	82	18

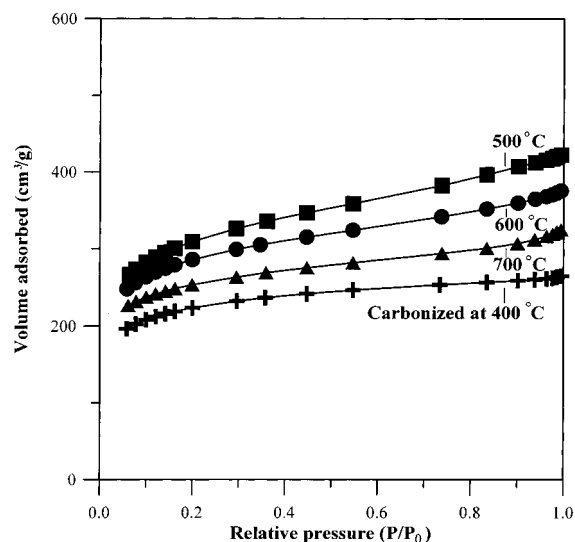
^a The chars were produced from carbonization of the 210–300 μm coals with ZnCl_2 at 500 $^\circ\text{C}$.

**Figure 3.** Adsorption isotherms of N_2 on BW activated carbons prepared from carbonization with ZnCl_2 at different temperatures for 1 h.

micropore fraction was slightly lower for the acid-washed carbons. This observation reveals that significant amounts of mesopores are still occupied by water-insoluble chemicals after the water-washing treatment. These mesopores became accessible to the nitrogen molecules as the carbons were treated with acid-washing to remove the water-insoluble chemicals.

It is obvious that the acid-washing process following carbonization with ZnCl_2 is necessary for the preparation of high-porosity carbons. Therefore, in the following discussion the acid washing was carried out on all the samples prepared from carbonization with ZnCl_2 .

Effect of the Carbonization Temperature. One of the advantages presented by the chemical activation of coals compared to the physical activation is the lower temperature of the process. The temperature range of carbonization employed in the present study was 400–700 $^\circ\text{C}$. The effects of carbonization temperature were examined. Figure 3 shows the N_2 adsorption isotherms on the carbons prepared from BW coal at different carbonization temperatures. The time for carbonization was 1 h. These isotherms show that the carbons are mainly microporous, but with a significant extent of mesoporosity. The adsorptive capacity is lowest for the

**Figure 4.** Adsorption isotherms of N_2 on MT activated carbons prepared from carbonization with ZnCl_2 at different temperatures for 1 h.

400 $^\circ\text{C}$ prepared carbon but reaches a maximum at 500 $^\circ\text{C}$. The increase in porosity by raising the carbonization temperature can be attributed to the release of tar (Ibarra et al., 1991). For carbonization temperatures above 500 $^\circ\text{C}$, the adsorptive capacity decreases with increasing temperature. The increase in temperature from 500 to 700 $^\circ\text{C}$ may induce a shrinkage in carbon structure, resulting in a reduction in porosity (Ahmadpour and Do, 1996). A temperature of 500 $^\circ\text{C}$ for ZnCl_2 activation has also been recommended by other workers (Kirubakaran et al., 1991).

The isotherms of the carbons from the MT coal are similar, and the results are shown in Figure 4. The data reveal that the trend of variation in adsorptive capacity with carbonization temperature is identical to that of the BW carbon. However, the BW carbon possesses a higher fraction of mesopores than the MT, since the plateau of the BW isotherm has a relatively higher slope. As discussed in our previous study on physical activation (Teng et al., 1996), the carbon coming from carbonization of the MT coal has a higher microporosity due to a higher oxygen content, which retards the caking of coal during carbonization.

The adsorption isotherms, such as shown in Figures 3 and 4, are employed to deduce the BET surface areas and pore volumes, and the results are shown in Table 3. As shown, both surface area and pore volume increase with the carbonization temperature to a maximum at 500 $^\circ\text{C}$ and then begin to decrease. The trends of the surface property variation with carbonization temperature are as expected, according to those revealed in the adsorption isotherms. However, one should notice that the maximum values of surface area and pore volume, which occur at 500 $^\circ\text{C}$ carbonization, are larger for the BW carbon than for the MT, although higher surface area carbons were produced from the MT by physical activation with CO_2 (Teng et al., 1996). Obviously, more sites are available in the BW structure for ZnCl_2 to promote the formation of cross-links, leading to the establishment of a rigid matrix and thus a high porosity. It is also interesting to notice that according to our previous study (Teng et al., 1997), the porosity of the carbon prepared from the BW coal can be significantly affected by oxidation, which would result in the formation of oxygen functional groups and then

Table 3. Effects of Carbonization Temperature on the Surface Properties of the Carbons from ZnCl₂ Activation^a

carboni- zation temp. (°C)	BET SA (m ² /g)	pore volume (cm ³ /g)	pore size distribution		average pore diameter (Å)
			micro (%)	meso (%)	
BW Carbon					
400	501	0.28	86	14	22
500	1300	0.83	75	25	25
600	895	0.55	77	23	24
700	858	0.49	83	17	23
MT Carbon					
400	775	0.41	90	10	21
500	1080	0.65	79	21	24
600	994	0.58	82	18	23
700	874	0.50	83	17	23

^a The time of carbonization was 1 h, and the particle sizes of the starting material were in the range of 210–300 μm .

form cross-links during carbonization, leading to a higher porosity with CO₂ activation. The oxidation effect was not as significant for the MT coal. It seems that the structure of the BW bituminous coal, which has a lower O/C ratio, has a higher tendency in forming cross-links, due to the impregnation of the dehydrogenation substances, such as ZnCl₂ and oxygen, into the coal structure.

However, as the carbonization temperature was further increased to above 500 °C, the porosity of the BW carbons became lower than that of the corresponding MT carbons. This result can be attributed to the fact that the MT coal has a larger amount of oxygen functional groups, which promote the cross-linking between coal structures to decrease the thermoplastic property during carbonization of a caking coal (Teng et al., 1996; Alvarez et al., 1994). The production of porosity in the carbons is related to the formation of cross-links between carbonaceous aggregates. Therefore, at higher temperatures it is suggested that the cross-links break, with a consequent rearrangement of carbonaceous aggregates and the collapse of pores. Since the BW carbon has a higher extent of porosity reduction resulting from the increase of carbonization temperature than the MT, it may suggest that the cross-links induced from the impregnation of ZnCl₂ are less thermally stable than those from the oxygen functional groups originally retained in the coals. In the study of physical activation with CO₂ (Teng et al., 1997), the cross-links induced from the oxygen functional groups introduced from oxidation treatment before carbonization were also found to be less resistant to heating than those from the oxygen originally retained in the coals.

Results in Table 3 also show that the BW carbon has a structure with a higher proportion of mesopores than the corresponding MT carbon. This is also true for the activated carbons prepared from physical activation with CO₂ (Teng et al., 1996). Obviously, oxygen retained in a bituminous coal retards caking and creates microporous structures during carbonization. This has been evidenced by other studies (Alvarez et al., 1994; Teng et al., 1997), showing that the macro/mesopore volume of the char decreases with an increasing extent of oxidation of the coal precursor and the micropore volume increases as the degree of oxidation increases. On the other hand, the results imply that the pores formed due to ZnCl₂ impregnation would have an average diameter larger than those induced from oxygen retained in coal.

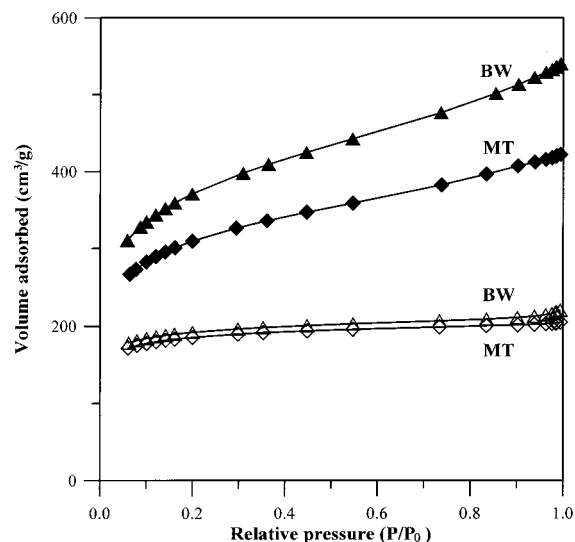


Figure 5. Adsorption isotherms of N₂ on the BW and MT activated carbons prepared from carbonization with ZnCl₂ at 500 °C for 1 h. Two different particle sizes of coals were used: 210–300 μm (solid symbols) and 400–1000 μm (empty symbols).

It can be seen from Table 3 that the pore diameter decreases from 25.4 Å at 500 °C to 22.8 Å at 700 °C for the BW carbon and from 24.0 to 22.7 Å for the MT. Obviously, upon carbonization with a higher temperature, the decrease in the average pore diameter is more severe for the BW carbon than for the MT. This observation is in agreement with the above implication that the BW carbon has a higher fraction of pores induced from the impregnation of ZnCl₂, and these pores are larger in diameter and less thermally stable than those induced from oxygen originally retained in the coal.

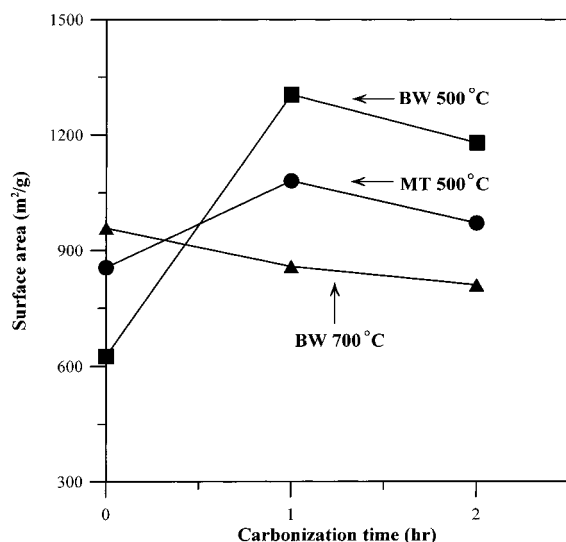
Effect of the Particle Size of Coal Precursors.

A different size of coal precursors, 400–1000 μm , was employed to prepare carbons for examining the effects of particle size on the surface properties of the resulting carbons. Figure 5 shows a typical comparison of the N₂ adsorption isotherms on the carbons prepared from the coals of different sizes. The samples were prepared by carbonization at 500 °C for 1 h. The isotherms reveal that the adsorptive capacity is much lower for the samples prepared from coals with a larger particle size. The surface structures of the samples from larger size coals are more microporous, as indicated by the more horizontal plateaus of the isotherms. The adsorption isotherms are employed to deduce the surface area and pore volumes. Table 4 shows the surface properties of the carbons prepared, at different carbonization temperatures, from the BW and MT coals with a particle size of 400–1000 μm . It can be seen that the variation of surface properties with the carbonization temperature is similar to that for the carbons prepared from the coals with a smaller particle size. Upon comparison with the results shown in Table 3, preparation of activated carbons from coals with a larger particle size results in the reductions in surface area and pore volume of the carbons. This can be attributed to the fact that the larger particles have less external surface area to contact with the chemical agent (Ahmadpour and Do, 1996) and/or a stronger resistance for intraparticle diffusion of the chemical agent. It can also be seen that the fraction of micropore volume is larger and the average pore diameter is smaller for the carbons prepared from the larger particle coals. This is probably

Table 4. Surface Properties of the Carbons from ZnCl_2 Activation at Different Carbonization Temperatures^a

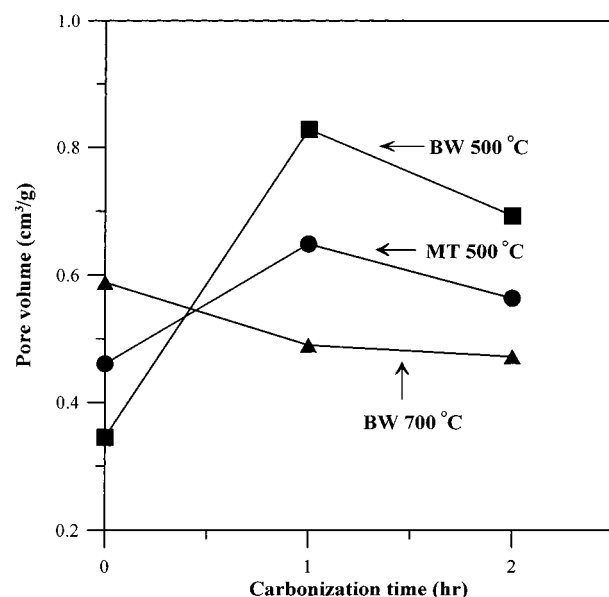
carboni- zation temp. (°C)	BET SA (m ² /g)	pore volume (cm ³ /g)	pore size distribution		average pore diameter (Å)
			micro (%)	meso (%)	
BW Carbon					
400	372	0.20	88	12	21
500	653	0.34	91	9	21
600	562	0.28	95	5	20
700	546	0.27	95	5	20
MT Carbon					
400	608	0.31	93	7	20
500	700	0.35	93	7	20
600	542	0.27	96	4	20
700	523	0.27	93	7	20

^a The time of carbonization was 1 h, and the particle size of the starting material was in the range of 400–1000 μm .

**Figure 6.** Carbonization time dependence of the surface area of the carbons prepared from activation with ZnCl_2 .

due to the lesser extent of ZnCl_2 impregnation for the larger particles, since it has been stated that ZnCl_2 impregnation generally induces the formation of pores with a larger average diameter than those from the oxygen retained in the coals.

Effect of the Carbonization Time. The influence of carbonization time on the developments of surface area and pore volume of the resulting carbons was also explored, and the results are shown in Figures 6 and 7, respectively. It can be seen from those figures that the influences of the carbonization time on the surface properties of the resulting carbons are different at different carbonization temperatures. For both BW and MT carbons prepared at 500 °C, the surface area and the pore volume show relatively low values when the carbonization process was performed by heating the samples from room temperature to 500 °C, followed by an immediate cooling (i.e., zero carbonization time). It has been reported that the basic char structure formed at about 500 °C for the carbonization of peach stones impregnated with ZnCl_2 (Caturla et al., 1991). Because of the high heating rate (30 °C/min) in the present study, it is likely that there was not enough time for the full development of porosity in the char structure, although the temperature, 500 °C, was high enough. The surface area and pore volume increased to a maximum as the carbonization at 500 °C continued for 1 h and then began to decrease for a longer carboniza-

**Figure 7.** Carbonization time dependence of the pore volume of the carbons prepared from activation with ZnCl_2 .

tion time. The decrease in porosity can be attributed to the caking of the structure with a prolonged heat treatment.

For the BW carbon carbonized at 700 °C, the surface area and pore volume decrease with the length of carbonization time, as revealed in Figures 6 and 7. Since the char structure has already been well formed at this temperature, the increase in carbonization time simply causes the break of the cross-links between carbon structures, with a consequent collapse of pores.

Comparison of the External Surfaces of the Resulting Carbons. The scanning electron micrographs of the external structures of the BW carbons prepared from physical and chemical activations were compared in Figure 8. The physical activation was performed by heating the coal from room temperature to 900 °C at 30 °C/min in N_2 , followed by a partial gasification (35% burn-off) of the resulting char in CO_2 at 900 °C. The surface area and the pore volume of this physically activated carbon are 360 m²/g and 0.19 cm³/g, respectively. About 90% of the pore volume of this carbon is contributed by micropores. The chemically activated carbon was prepared by carbonization with ZnCl_2 at 500 °C for 1 h. The surface properties of this carbon have been presented in Table 3.

It can be seen from the micrographs that the physically activated carbon, as shown in Figure 8a, has an intact external structure, while the external surface of the chemically activated carbon, as shown in Figure 8b, is full of cavities. The reason for the formation of the cavities on the ZnCl_2 -activated carbon is not clear. According to the micrograph of Figure 8b, it seems that the cavities resulted from the evaporation of ZnCl_2 during carbonization, leaving the space previously occupied by the ZnCl_2 . The carbonization temperature for chemical activation was too low to cause the agglomeration of the char structure. Since the carbonization temperature was high for the physical activation (900 °C), caking and agglomeration occurred on char structures and thus resulted in the formation of chars with an intact external surface, as revealed in Figure 8a. Because of the void structure, mechanical properties, such as hardness and abrasion resistance, should be

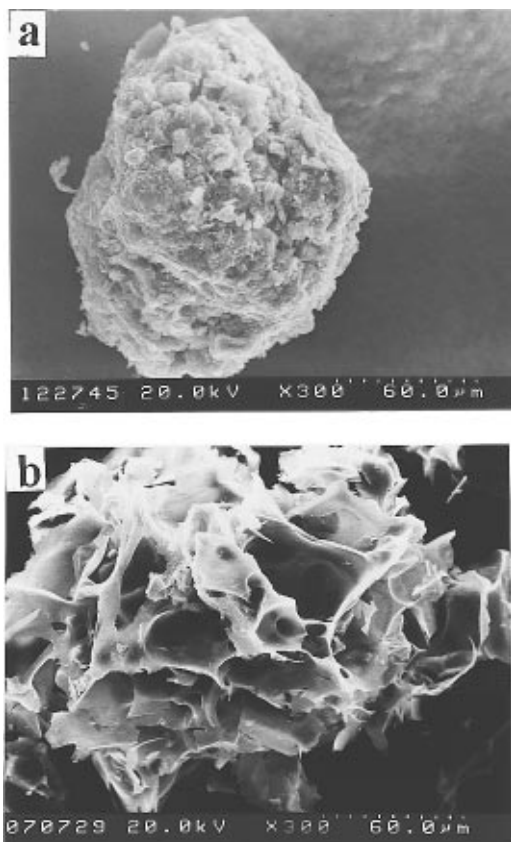


Figure 8. Scanning electron micrographs of the carbons prepared from (a) physical activation with CO_2 at 900 °C and (b) chemical activation with ZnCl_2 at 500 °C.

carefully evaluated for producing activated carbons from bituminous coals with ZnCl_2 activation.

Conclusions

This study has demonstrated that ZnCl_2 is a suitable activating agent for the preparation of high-porosity carbons from bituminous coals. The surface area and the pore volume of the carbon produced by ZnCl_2 activation can be as high as 1300 m^2/g and 0.83 cm^3/g , respectively.

The carbonization behavior of the ZnCl_2 -treated coal was compared with that of the untreated coal. For the carbonization of the ZnCl_2 -treated sample, the release of moisture and ZnCl_2 represents most of the evolution, indicating that ZnCl_2 plays an important role in retarding tar escape during carbonization.

The washing process following carbonization with ZnCl_2 has a significant influence on the surface properties of the resulting char. It was found that acid washing is a necessary step for the preparation of high-porosity carbons.

The porosity of the resulting char increased with the carbonization temperature to a maximum at a temperature of 500 °C and then began to decrease with the temperature. Analysis of surface structure variation with the temperature suggests that the cross-links induced from the impregnation of ZnCl_2 are less thermally stable than those from the oxygen originally retained in the coal.

The maximum values of the surface area and the pore volume are larger for the coal with a lower O/C ratio. It is suggested that more sites are available in this coal for ZnCl_2 to promote formation of cross-links, leading

to a higher porosity. The carbon prepared from the coal with a lower O/C ratio was found to have a structure with a larger proportion of mesopores.

An increase in particle size of the coal precursors leads to a reduction in surface area and pore volume of the resulting carbons. This may be attributed to the fact that the larger particles have less external surface area to contact with the chemical agent and/or a stronger resistance for intraparticle diffusion of the chemical agent.

The effects of the carbonization time on the surface properties of the resulting carbons are different at different carbonization temperatures. At a carbonization temperature of 500 °C, 1 h of carbonization is recommended for preparing a high-porosity carbon. At 700 °C, the porosity decreases with the length of carbonization time.

A scanning electron microscopic study shows that a physically activated (CO_2 -gasified) carbon has an intact external structure, while the external surface of a chemically activated (ZnCl_2 -treated) carbon is full of cavities. The mechanical strength of the chemically activated carbon should be carefully examined because of its void structure.

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Literature Cited

- Ahmadpour, A.; Do, D. D. The Preparation of Active Carbons from Coal by Chemical and Physical Activation. *Carbon* **1996**, *34*, 471.
- Alvarez, T.; Fuertes, A. B.; Pis, J. J.; Parra, J. B.; Pajares, J.; Menéndez, R. Influence of Coal Oxidation on the Structure of Char. *Fuel* **1994**, *73*, 1358.
- Bansal, R. C.; Donnet, J. B.; Stoekli, H. F. *Active Carbon*; Marcel Dekker: New York, 1988.
- Caturla, F.; Molina-Sabio, M.; Rodríguez-Reinoso, F. Preparation of Activated Carbon by Chemical Activation with ZnCl_2 . *Carbon* **1991**, *29*, 999.
- Greenbank, M.; Spotts, S. Six Criteria for Coal-Based Carbons. *Water Technol.* **1993**, *16*, 56.
- Ibarra, J. V.; Moliner, R.; Palacios, J. M. Catalytic Effects of Zinc Chloride in the Pyrolysis of Spanish High Sulphur Coals. *Fuel* **1991**, *70*, 727.
- Illán-Gómez, M. J.; García-García, C.; Salinas-Martínez de Lecea, C.; Linares-Solano, A. Activated Carbons from Spanish Coal. 2. Chemical Activation. *Energy Fuels* **1996**, *10*, 1108.
- Kirubakaran, C. J.; Krishnaiah, K.; Seshadri, S. K. Experimental Study of the Production of Activated Carbon from Coconut Shells in a Fluidized Bed Reactor. *Ind. Eng. Chem. Res.* **1991**, *30*, 2411.
- Laine, J.; Yunes, S. Effect of the Preparation Method on the Pore Size Distribution of Activated Carbon from Coconut Shell. *Carbon* **1992**, *30*, 601.
- Muñoz-Guillena, M. J.; Illán-Gómez, M. J.; Martín-Martínez, J. M.; Linares-Solano, A.; Salinas-Martínez de Lecea, C. Activated Carbons from Spanish Coal. 1. Two-Stage CO_2 Activation. *Energy Fuels* **1992**, *6*, 9.
- Rodríguez-Reinoso, F.; Molina-Sabio, M.; González, M. T. The Use of Steam and CO_2 as Activating Agents in the Preparation of Activated Carbons. *Carbon* **1995**, *33*, 15.
- Ruiz Beviá, F.; Prats Rico, D.; Marcilla Gomis, A. F. Activated Carbon from Almond Shells. Chemical Activation. 2. ZnCl_2 Activation Temperature Influence. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 269.
- Sircar, S.; Golden, T. C.; Rao, M. B. Activated Carbon for Gas Separation and Storage. *Carbon* **1996**, *34*, 1.

Teng, H.; Ho, J.-A.; Hsu, Y.-F.; Hsieh, C.-T. Preparation of Activated Carbons from Bituminous Coals with CO₂ Activation. 1. Effects of Oxygen Content in Raw Coals. *Ind. Eng. Chem. Res.* **1996**, 35, 4043.

Teng, H.; Ho, J.-A.; Hsu, Y.-F. Preparation of Activated Carbons from Bituminous Coals with CO₂ Activation—Influence of Coal Oxidation. *Carbon* **1997**, 35, 275.

Wigmans, T. Industrial Aspects of Production and Use of Activated Carbons. *Carbon* **1989**, 27, 13.

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