THE PRODUCTION OF ACTIVATED CARBONS FROM COALS BY CHEMICAL ACTIVATION

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ABSTRACT
Activated carbons prepared from coals by chemical means using phosphoric acid as the activant have a dominantly microporous adsorptive capacity which develops up to 450 °C. Chemical activation promotes carbonization at lower temperatures than is obtained thermally and is effective in removing sulfur, mainly as hydrogen sulphide. Reducing the ash content of a bituminous coal by cleaning prior to activation has beneficial effects upon surface area development.

INTRODUCTION
Coals are widely used as feed-stocks for activated carbons produced by "thermal" methods, i.e., by carbonization followed by reaction with oxidizing gases (e.g., steam or carbon dioxide) at elevated temperatures. By contrast, the preparation of activated carbons from coals by "chemical" activation (i.e., by reaction with an ionic reagent at lower temperatures than are used for thermal activation) has been little studied. Chemically-activated carbons are commercially produced from cellulosic precursors using zinc chloride or phosphoric acid as activants (1), but here too there is little fundamental understanding of the chemistry of the conversion processes.

The objectives of the present work are to investigate the potential of coals of different rank as precursors for the production of active carbons using phosphoric acid as the activant. Specific aims are to relate the development of porosity in the carbons to the structure of the precursor and to the chemical and morphological changes. In this paper we report a study using a subbituminous coal and a bituminous coal as precursors, including some results of pre-cleaning the bituminous coal using flotation.

EXPERIMENTAL
Chemical Activation.
The sub-bituminous coal is mined from the Wyodak seam in Wyoming (designated: Wyodak coal) and the bituminous coal was selected from the Illinois Coal Basin Sample Program (designated IBC 101 coal); chemical analyses of the coals are shown in Table 1.

The ground coals (-850 μm) were reacted with 50% phosphoric acid in two temperature stages. For the Wyodak coal, the first stage involved refluxing a coal-acid mixture (4:1 ratio of acid solution to coal) for 60 min, following which the slurry was concentrated by evaporation (maximum temperature, about 130°C). In the second stage, the slurry was heat treated in a stainless steel reactor, under flowing nitrogen at atmospheric pressure and held for 60 min at a final heat treatment temperature (HTT) between 350 and 650°C.

For the IBC 101 coal, the first stage procedure was modified: a coal-acid slurry (30 ml acid:20 g of coal) was heated to 170 °C in the same reactor, and held at this temperature for about 30 minutes before heating to the final HTT. The content of H_2S released as gas was monitored with a HACH Carle gas chromatograph using standard procedures for calibration. The solid products were leached with distilled water to pH = 6 and vacuum dried at 110 °C for further analysis. For comparison, parallel series of carbonized coals were prepared by heat treatment for 1 h in flowing nitrogen (80 ml/min) at the same HTT values.

Coal cleaning.
Clean coal samples have been produced using a laboratory scale flotation unit. In a typical arrangement, fuel oil or pentane is vigorously mixed with a coal/water slurry to render the coal particles hydrophobic and to selectively agglomerate them. The agglomerated slurry is then screened; the free ash particles flow through the screen and agglomerated coal is retained.

Characterization.
Elemental analyses of the carbons were carried out using standard methods. The carbons were also examined using Fourier transform infra red spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). FTIR spectra were acquired using a NICOLET 20 SXC spectrometer at 4 cm^{-1} resolution. Pressed KBr pellets at a sample/KBr weight ratio of 1:200 were scanned and then normalized to 0.5 mg. Spectral subtractions were conducted on an equivalent weight basis. XPS analysis of the coal samples was carried out in a Leybold-Heraus LH-11 spectrometer equipped with a hemispherical analyzer using Mg Kα radiation (1253.6 eV) at a pass energy of 100 eV. The powdered coal samples were pressed into a thin wafer and were placed on a stainless steel sample holder using a conductive adhesive. The spectra obtained in all regions have been referenced to C1s at 284.3 eV (BE). The identification of the various chemical species has been carried out using NIST XPS Database Version 1.0 and standard compounds. Pore structure characterization was carried out using nitrogen adsorption at 77K using an Autoscan 6 automated adsorption apparatus.

RESULTS

Chemical and Structural Changes

Comparison of the thermally-treated and chemically-activated carbons, Table 1, shows that acid-treatment of both coals causes a more rapid increase in carbon content and reduction in H/C atomic ratio with increasing HTT, which are more pronounced at lower HTT. The ash contents of carbons from both precursors increase with HTT, but those for the acid-treated products are much higher, particularly at HTT > 450°C, and correlate with increases in P content. For both coals, acid-treatment up to HTT = 650 °C releases about 75% of the sulphur in the original coal, Table 1, mainly as H_2S, e.g., Figure 1. The release of sulfur as H_2S from the thermally-carbonized series shows a similar trend to that observed by Khan (2).

The FTIR spectra for the IBC 101 coal and the chemically-activated carbons are shown in Figure 2. There is a strong band at 2914 cm^{-1} in the parent coal, due to aliphatic C-H stretch, which decreases at HTT = 350°C, while the band at 3040 cm^{-1} due to aromatic C-H stretch intensifies, suggesting that aromatization may be occurring. The band appearing at 1690 cm^{-1} after HTT = 350°C is due to carbonyl (C=O) groups. It weakens in intensity at HTT = 550°C and disappears at HTT = 650°C. Carbonyl groups have also been found both in Sutcliffe Speakman 110 activated carbon (3) and in carbons produced by activation of coconut shell with phosphoric acid (4). The difference spectrum obtained by subtracting the spectrum of the thermally-treated sample from that of the acid-treated sample at HTT = 450°C (Figure 3) suggests that the coal is oxidized by chemical activation. For the chemically-activated carbons a particularly strong band appears at 1180 cm^{-1} at HTT = 450°C, 550°C and 650°C. The origin of this band is uncertain. It may be due either to additional C-O stretch, or to P=O groups attached to an aromatic structure. The source of the 1180 cm^{-1} band is being investigated.

Compilations of the C1s and P2p XPS spectra obtained from the chemically-activated carbons from IBC 101 coal after various HTT are in Figure 4; these spectra have been de-convoluted into component peaks. The C1s spectra, Fig. 4(a) to 4(e), have been fitted to four component peaks. The most intense peak, ca. 284.3 eV, is attributed to graphitic-type carbon species; the second peak at ca.285.8 eV may be due to organophosphate species; the third peak at ca. 287.9 eV coincides with that of carbonyl groups, in agreement with the FTIR results; the fourth peak at ca. 289.1 eV is due to carbonate groups. The prominent peaks at ca. 133.5 eV and ca. 135.3 eV in P2p spectra, Fig. 4(a)'-(b)', are attributed to inorganic hydrophosphate groups and to P_2O_5 respectively. When HTT increases from 350 to 450 °C, the hydrophosphate intensity decreases and there is a corresponding increase in the P_2O_5 intensity, suggesting a dehydration process. At HTT = 550 and 650 °C, the hydrophosphate and P_2O_5 peaks are

still present, but two additional peaks appear whose origins are uncertain. The peak at ca. 131.6 eV could either be due to a phosphide of a transition metal or to a phosphorous compound in association with organic sulfur species. The peak at ca. 136.1 eV may be due to a P-containing species in a high oxidation state; work on the identification of these peaks is continuing.

Pore Structure Characterization

BET surface areas, S_{BET}, were obtained from the nitrogen adsorption isotherms for the activated carbons. The isotherms were also analyzed by the α_s method (5) to yield non-microporous surface areas, S'_{BET}, and micropore volumes, V_o, Table 2. Both carbon series are dominantly microporous, although the development of microporosity is more extensive for the carbons produced from the Wyodak coal. The extents of mesoporosity in the two series (indicated by S'_{BET} values) are comparable for HTT > 450 °C. For both carbon series S_{BET} and S'_{BET} pass through maxima below HTT = 650°C, as observed by others (4). However, the effect of HTT on surface area is obscured by the substantial ash contents of the activates, Table 1. Assuming that the ash makes a negligible contribution to nitrogen adsorption, the surface areas can be recalculated on a dry, ash-free (daf) basis, Table 2. The corrected data show that, for the Wyodak coal series, the maximum in S_{BET} is shifted to a higher HTT, while, for the IBC coal series, the maximum disappears (or is possibly shifted to HTT > 650 °C). S_{BET} values for the thermally-treated coals (not shown in Table 2) increase with HTT up to 50 m^2/g for the Wyodak coal series and up to 24 m^2/g for the IBC 101 coal series. The results indicate that the thermally-treated carbons contain narrow micropores and negligible mesoporosity.

The data in Tables 1 and 2 show that coal cleaning by flotation substantially reduces the ash content of the parent IBC 101 coal by 61%; the ash content of the chemically-treated carbon produced from the cleaned coal at HTT = 550 °C is reduced by 55% when compared with that for the activate formed from the parent coal at the same HTT. Table 2 shows that coal cleaning produces a significant increases in both S_{BET} and S'_{BET}.

DISCUSSION

Chemical analyses and FTIR results show that phosphoric acid treatment of the coals promotes aromatization and carbonization at low HTT. Evidence for accelerated carbonization is also provided by reflectance measurements on the subbituminous coal (6). The processes occurring during the reaction of phosphoric acid at low temperatures are probably analogous to acid-catalyzed cracking reactions in coal liquefaction using Lewis acids. Acid catalysts can promote rupture of methylenic, etheric and thioetheric linkages between cyclic structures in coal by ionic mechanisms which involve protonation followed by bond scission (7). Proton donation from phosphoric acid to aromatic

entities, -Ar-, in the coal structure is consistent with the XPS evidence for inorganic hydrophosphates; the reactions can be represented as:

$$\cdots\text{-Ar-}\cdots + H_3PO_4 = \cdots\text{-(ArH)}^+\text{-}\cdots + H_2PO_4^-.$$

In the present case, it is likely that bond scission will be followed by rapid condensation of aromatic fragments to form a strongly cross-linked solid product at much lower temperatures than are required for thermal decomposition of the coal. The indications from FTIR and XPS for the presence of organophosphorus entities suggest that direct reactions between phosphoric acid and the coal structure also occur, particularly at high temperatures. The formation of an extensive cross-linked network at low temperatures in the chemical activation process may be linked to the early development of significant open microporosity. By contrast, the condensation processes which accompany thermal carbonization occur at much higher temperatures and lead to significant shrinkage and formation of a closed micropore network which can only be developed by subsequent thermal activation.

CONCLUSIONS

There are clear differences in porosity development between the thermally-carbonized and chemically-activated coals, which reflect differences in structural development. Acid-treatment causes the rupture of linkages in the coal structure, leading to adduction and the early development of a strongly cross-linked solid product. This process is accompanied by the development of high surface areas at moderate HTT. Work on elucidating the mechanisms of the chemical activation process is continuing.

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REFERENCES

1. Smisek, M. and Cerny, S. Active Carbon Manufacture, Properties and Applications, Elsevier, Amsterdam, 1970.
2. Khan, M. R., Fuel, 1989, **68**, 1439.
3. Meldrum, B.J. and Rochester, C.H., Fuel, 1991,**70**, 57.
4. Laine, J., Calafat, A. and Labady, M., Carbon, 1989, **27**, 191.
5. Rodriguez-Reinoso, F., Martin-Martinez, J-M., Prado-Burguette, C.and McEnaney, B., J.Phys. Chem., 1987, **91**, 515.
6. Derbyshire, F. J., Jagtoyen, M., McEnaney, B., Rimmer, S. M., Stencel, J. M. and Thwaites, M. W. Proc. 20th Biennial Carbon Conference, 23-28 June, 1991, Sta. Barbara, CA., in press.
7. Derbyshire, F.J., Catalysis in Coal Liquefaction., IEA Coal Research, London, 1988, pp. 29-36.

TABLE 1. CHEMICAL ANALYSIS OF COALS AND CARBONS (wt%)

Material	HTT	C	H	N	S	P	Ash
	(°C)			(daf)			(mf)
Wyodak coal							
Parent coal		74.3	5.0	1.0	1.2	0.03	8.2
Thermally	350	77.7	3.8	1.2	1.1	0.01	8.0
treated	450	82.6	2.9	1.3	0.9	0.01	9.3
carbons	550	91.6	2.0	1.5	1.2	0.01	11.9
	650	94.1	1.5	1.4	1.2	0.3	11.9
Chemically	350	87.7	2.3	1.2	0.8	1.4	9.7
treated	450	91.1	1.7	0.9	0.5	1.4	7.3
carbons	550	94.4	1.3	0.9	0.3	4.7	17.6
	650	94.6	0.4	1.1	0.3	4.4	15.9
IBC 101 coal							
Parent coal		79.8	5.2	1.4	5.2	0.0	10.5
Thermally	350	78.8	4.9	1.4	4.6	0.01	10.2
treated	450	86.5	3.1	1.7	3.7	0.01	13.6
carbons	550	91.1	2.2	1.9	4.7	0.01	15.1
Chemically	350	87.1	3.8	1.5	2.9	2.5	15.8
treated	450	86.9	2.5	1.2	1.6	5.1	26.6
carbons	550	93.4	1.4	1.4	1.2	3.9	20.8
	650	102.7	0.9	1.4	1.2	7.2	31.1
Cleaned parent		78.0	5.2	1.4	4.4	0.03	4.1
Clean carbon	550	88.9	1.9	1.1	0.9	1.5	9.2

TABLE 2. ADSORPTION PARAMETERS FOR CHEMICALLY-ACTIVATED CARBONS

Precursor	HTT (°C)	S_{BET} (m^2g^{-1})	S'_{BET} (m^2g^{-1})	V_o (cm^3g^{-1})	S_{BET} (daf)	S'_{BET} (daf)
Wyodak coal	350	416	31	0.17	461	34
	450	791	54	0.32	853	58
	550	731	47	0.30	887	57
	650	718	34	0.30	854	40
IBC 101 Coal	350	2	1	>0.01	2	1
	450	401	25	0.14	546	34
	550	575	56	0.20	726	71
	650	539	46	0.19	782	67
Cleaned coal	550	638	96	0.21	703	106

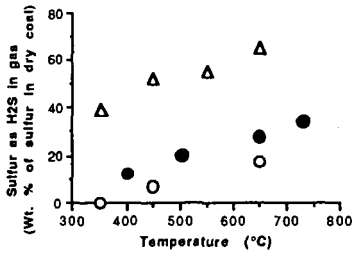

Figure 1. Liberation of sulfur as H2S

This work: △ (acid treated coal), ○ (no acid treatment)

● Khan (2), (no acid treatment)

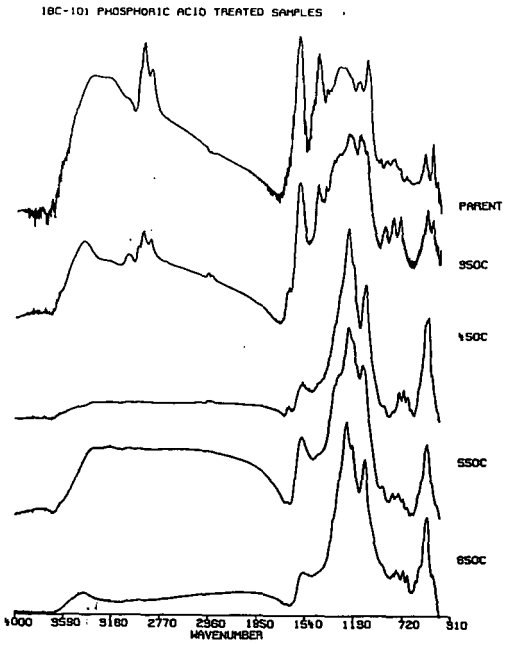

Figure 2. Infrared spectra of activated carbon prepared by chemical activation with phosphoric acid at 350, 450, 550 and 650°C along with parent coal.

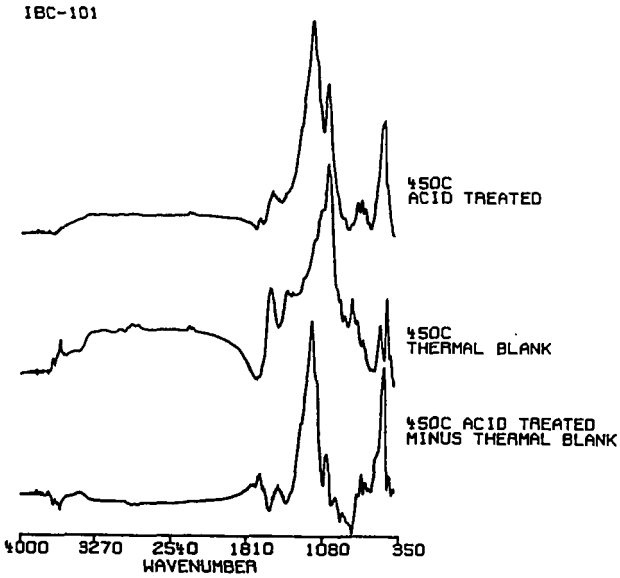

Figure 3. Infrared spectra of chemically activated carbon and thermally carbonized carbon at 450°C and a difference spectrum of chemically activated carbon minus thermal blank.

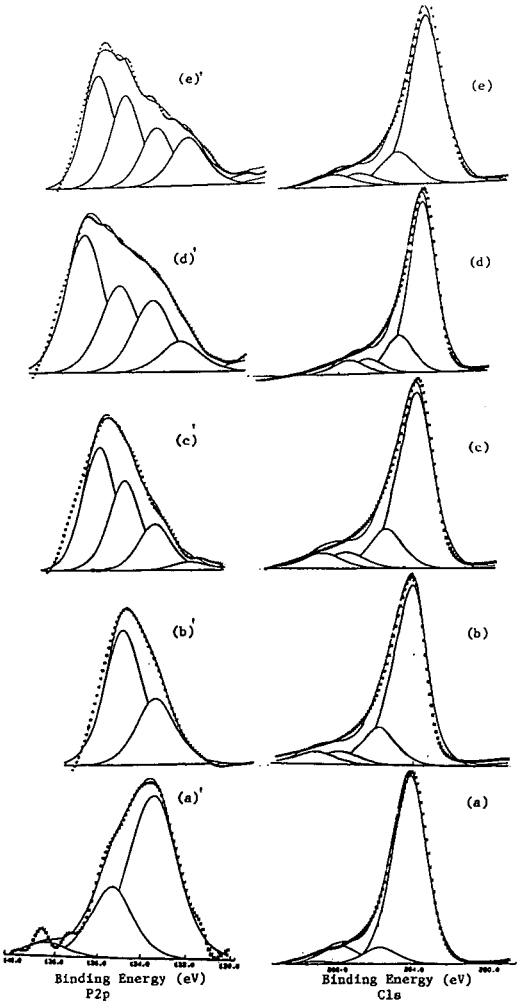

Figure 4. XPS spectra for carbons produced from IBC 101 coal. HTT(°C): 350 (a)(a'); 450 (b)(b'); 550 (c)(c'); 550 (cleaned coal) (d) (d'); 650 (e)(e').