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A Surface Area/Porosity Investigation of Four Coals:
Upper Freeport; Illinois no. 6; New Zeland, Stockton; and Panther Valley

by

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Introduction

This project had as its primary objective the establishment of the specific surface areas (SSAs) and the qualitative definition of any existing pore structure of four coal samples supplied by Dr. Robert Good of the Chemical Engineering Department of the State University of New York at Buffalo. The samples included three bituminous coals (Upper Freeport, Illinois No. 6 and New Zealand Stockton) and one Anthracite (Panther Valley Mine).

Previous literature (1,2,3,4,5,6,7) indicates that measurement of SSAs by nitrogen adsorption at liquid nitrogen temperatures do not give valid values. Typical results show near zero surface areas and it is necessary to utilize carbon dioxide as an adsorbate at or from around -78°C to room temperature. The ability of CO_2 , as opposed to N_2 to measure SSAs of coals is ascribed to the much lower activation energy of diffusion (1,2,3,4) of CO_2 in the ultrafine microporous structure reported.

Two other explanations are possible. One is that the greater ease of CO_2 penetration opens up defect structure and can create additional pore structure. If this were the case, nitrogen adsorption following that of CO_2 should detect the newly formed porosity. The other possibility is that there is essentially no pore structure and that CO_2 is sorbed or absorbed into the coal structure while N_2 is not. If CO_2 absorption were taking place then equilibrium would be virtually unattainable at any temperature until saturation took place.

In addition to obtaining SSAs for the coals examined, our intention was to evaluate the current rationalizations given for the use of CO_2 as an adsorbate.

Experimental

Two high vacuum systems were utilized in this study and are illustrated in Figures 1 and 2. In Figure 1 the system is a high vacuum, gravimetric microbalance adsorption system and was used for the study of the first coal examined: the Upper Freeport sample. The system can accommodate a sample size approaching one gram and can detect weight changes of approximately one microgram. Pressures of the adsorbate could be controlled from zero to one at atmosphere. Nitrogen adsorption was carried out at -196°C (liquid nitrogen temperature) while CO_2 adsorption was at -78°C utilizing a solid CO_2 -acetone slurry. Further details of this system have been published elsewhere (8). A 500 mg sample of the coal was utilized in granular form (60-80 mesh). Degassing the sample at room temperature ($\sim 23^{\circ}\text{C}$) or at 125°C made little difference to the N_2 adsorption isotherm. Adsorption was studied in the sequence: N_2 , CO_2 , N_2 .

The second high vacuum system was used for the other three samples and was a modified BET volumetric system; details have been published elsewhere (9). This is illustrated in Figure 2. Since, again, the temperature of outgassing made little difference to the adsorption isotherm, 125°C outgassing was selected. While outgassing at 125°C increased water vapor removal it also caused a small increase in the degassing of volatile hydrocarbons possibly affecting the chemical nature of the coal. Only the Illinois #6 coal showed significant hydrocarbon degassing at 125°C .

Electron micrographs were obtained on a Hitachi S800 field emission scanning electron microscope. The instrument had a theoretical resolution of $20 \text{ \AA}$ at 25 KV.

Results and Discussion

N₂ Adsorption

Adsorption data on all four coals are shown in Figure 3 and are plotted as cc STP Vs Relative Pressure. It will be immediately seen that for three of the coals (New Zealand Stockton, Panther Valley Mine and Upper Freeport) the amounts of N₂ adsorbed are almost within experimental error of zero adsorption except at or close to saturation vapor pressure. Equilibrium times for nitrogen adsorption were of the order of minutes except at saturation vapor pressure when even temperature shifts of less than 0.1°C caused significant weight changes and non-equilibrium conditions. The adsorption at that point is essentially that of external surface condensation. For the remaining coal (Illinois #6) however a characteristic S-shaped (BET Type II) isotherm is obtained indicating that nitrogen "sees" significant micro and mesopore structure in this coal. Equilibrium times here were considerably greater than for the other three coals, being of the order of hours rather than minutes.

It is important to note that although CO₂ saw different (larger) SSAs for all four coals, subsequent reevaluation by N₂ showed no change. It would appear that while CO₂ can detect internal surface structure not seen by nitrogen, the reverse is not always the case.

The SSAs for all four coals, using 16.2 Å²/N₂ molecule and the BET equation (10):

$$\frac{x}{n(1-x)} = \frac{1}{cn_m} + \frac{(c-1)x}{cn_m}$$

where n_m is the number of moles adsorbed, n_m the number at monolayer coverage, C is a constant, and x the relative pressure, are listed in Table 1.

CO₂ Adsorption

Adsorption data for all four coals are shown in Figure 4 and are plotted as cc STP Vs. Relative Pressure. In every case the amounts adsorbed were substantially greater than that for N₂. Indeed any N₂ adsorption prior to (SVP) is essentially negligible except in the case of Illinois #6. Equilibrium times for CO₂ adsorption were, in all cases, of the order of days rather than hours. Typically 2-3 days were necessary between the points indicated. In view of this situation and the relatively high SVP of CO₂, data were taken at low relative pressures only, though sufficiently high to satisfy the "suitable" range of relative pressures (0.05 to 0.30) for the BET equation (10). It should be noted that although the rate of CO₂ adsorption at -78°C is extremely slow, nevertheless equilibrium finally was established. For the CO₂ area/molecule values of 17.0 Å² and 22.1 Å² were used. The former is a closed packed calculated (11) value while the latter (12) was obtained by comparing N₂ and CO₂ values on a number of coals at -78°C and is probably more realistic.

Electron Microscopy

Powdered samples of two coals were studied with the Hitashi field emission scanning electron microscope. Each sample was coated to about 50Å depth with carbon to reduce surface charging. The two coals were selected as examples of one which had a very low N₂ surface area (Upper Freeport) and one with a measurable N₂ surface area (Illinois #6).

For the Upper Freeport coal magnifications ranged from 10K to 150K. In figures 5a through 5d the lower part of each micrograph represents a further five fold magnification. Care was taken to select regions of representative appearance so that an adequate surface survey was performed. Figures 5a,b,c show little other than rough surfaces and smooth glassy fractures. There is some suggestion of particle fusion and slight macroporosity in figure 5d. Figures 5e,f at 50 and 150K lack any indication of macro- or mesoporosity whatsoever, with 5e revealing a glassy surface and 5f a slight surface roughness.

Turning to the Illinois #6 sample, while regions of glassy fractured surfaces are evident (Figure 6a,b), significant macroporosity is also evident in Figures 6c,d. At higher magnification (100K) indication of some small degree of mesoporosity is still evident (Figures 6e,f).

While the electron micrographs do not quantitatively define the pore structure of these samples, they are qualitatively consistent with the surface area findings listed in Table 1 and those for other Illinois coals (12). The results are also similar to those obtained with another bituminous coal (5) where a similar range of porosity was revealed using transmission electron microscopy on specially prepared thin sections.

Summary

The currently accepted thought on the different sorption behavior of N_2 and CO_2 on/in coal samples would appear to be essentially correct: that the lower activation energy of CO_2 in penetrating defect or ultrafine micropore ($<5\text{\AA}$ width or diameter) structure enables it to "read" the surface area. The failure of an $N_2/CO_2/N_2$ sorption sequence to show significant increased surface area on the second nitrogen-adsorption shows that the CO_2 has not

created the surface area it sees. In addition, while CO_2 equilibrium times were long at -78°C , equilibrium was attained in days. Were bulk solubility significant equilibrium times would be much longer and the isotherm curvature, typical of reduced available area with increasing pressure, would not be found in the observed isotherms. There are, however, problems associated with the use of CO_2 as an adsorbate. The high quadrupole moment of CO_2 ($3.1\text{--}3.4 \times 10^{-26}$ esu) results in a considerable sensitivity to the presence of polar groups. Chemisorption also may occur. These considerations mean that the SSAs obtained may well reflect not only the actual surface areas but also the differing degrees of polarity of the coal samples.

In the special case of the Illinois #6 coal, adsorption in the entire micropore, mesopore and macropore range takes place. While other coals of similar nature (5,12) show similar behavior, we do not have sufficient information to identify the precise physical and chemical characteristics that produced the significantly different pore structure.

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Table 1

Specific Surface Areas of Four Supplied Coal Samples

<u>Sample</u>	<u>Nitrogen(m²/g)</u> (16.2 Å ² /molecule)	<u>Carbon Dioxide(m²/g)</u> (17.0 and 22.1 Å ² /molecule)	
Upper Freeport	.4	49.0	63.7
Illinois #6	23.4	78.9	102.6
New Zealand Stockton Coal	0.4	44.8	58.2
Anthracite Panther Valley Mine	0.4	73.8	95.9

Figure 1

high-vacuum beam microbalance system. ○ represents a one-way stopcock;

●, two-way. All other sections are self-evident or are as follows:

1. A Pd-Ag alloy thimble for H₂ purification.
2. Liquid nitrogen trap.
3. Two-stage mercury diffusion pump.
4. Ballast chamber.
5. Two-stage rotary oil pump.
6. Drying tube.
7. Liquid adsorbate holder.
8. UHV valve.
9. Handgown tubes (see Fig. 7 for details of sample hangdown tube).
10. Vacuum-tight electrical feedthrough.
11. A Texas Instruments Bourdon spiral gauge.
12. Ionization gauge.

Figure 2- VOLUMETRIC GAS-ADSORPTION APPARATUS

Nitrogen Adsorption on Specified Coal Samples

Figure 3

Carbon Dioxide Adsorption on specified Coal Samples

Figure 4

Fig. 5a

Fig. 5b

Fig. 5c

Fig. 5d

Fig. 5e

Fig. 5f

The magnification is stated for each micrograph and the actual size of features stated in conjunction with the broken line magnitude bar.

Fig. 6a

Fig. 6b

Fig. 6c

Fig. 6d

Fig. 6e

Fig. 6f

The magnification is stated for each micrograph and the actual size of features stated in conjunction with the broken line magnitude bar.

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