

A Possible Connection Between Gas Solubility in Coals and BET Surface Areas

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INTRODUCTION

Gas adsorption techniques have been widely used in determining surface areas of porous and nonporous solids. The surface areas of coals, calculated from nitrogen isotherms at 77.8°K, are considerably less than those obtained using CO₂ at 195°K.^{1,4} It is generally believed that N₂ yields low surface areas because the micropores in the coals are not completely accessible to N₂ at 77.8°K. Limitations are imposed by an activated diffusion process for N₂ and/or shrinkage of the coal pores at 77.8°K.^{1,4} Carbon dioxide has a lower activation energy for adsorption than N₂.^{1,5,6} It has been suggested that CO₂ interacts with oxygen functionalities in coals resulting in swelling which may contribute to the large surface areas for coals.

As part of another investigation, we have measured BET surface areas of a high volatile bituminous coal with small hydrocarbon gases expected to be insoluble in the coal. We report here a comparison of these surface areas with those obtained using CO₂ and Ar. We tentatively conclude that the solubility of CO₂ in coals is important in that it gives CO₂ access to closed pores which are otherwise ignored in surface area measurements by gas adsorption. It may be that the majority of the coal surface area lies in closed pores.

EXPERIMENTAL

A high volatile Ill. No. 6 coal sample (100 mesh, 75.2% C, 4.5% H, 1.4% N, 3.3% O, 2.4% S all dmmf) was obtained from the Premium Coal Sample Bank at Argonne National Laboratory. 100 mg samples of this coal were transferred into a preweighed sample container in a nitrogen filled glovebox for each experiment. The samples were outgassed on a glass BET isothermal apparatus under a vacuum of approximately 10⁻³ torr for no less than 8 hrs. A Datametrics Barocel pressure sensor was used to measure the pressure drop from a known volume to the sample container. The dead volume of the sample container was determined by the pressure difference of He from the known volume to the sample container at 77.8°K. This instrument has given correct surface areas for standard materials.

RESULTS AND DISCUSSION

The surface areas we obtained using Ar and CO₂ (Table I) are consistent with those reported for Ill. No. 6 coal by others.^{2,4} The astounding feature of the data in Table I is the very low surface area obtained with cyclopropane. It is considerably less than the surface area given by CO₂. Cyclopropane and CO₂ have the same cross-sectional area when they are determined by the method of Emmett and Brunauer. The cross-sectional area of cyclopropane₂ calculated from its structure and standard bond lengths is 23.2 Å² if it lies flat and 20.3 Å² if it lies on a side. These are close enough to the calculated value and to each other to have no effect on our conclusions. Since the molecules are of similar size, it is difficult to rationalize the very large surface area differences using arguments based on molecular sieving by the pore system. When an adsorbate molecule is soluble in the coal, the surface area increases with solubility (Fig. I, work by Reucroft and Patel, ref. 2). On this basis, it is possible that the low surface areas observed with nitrogen (Table II), CCl₄, and n-hexane (Fig. I) are all correct and the surface area obtained from CO₂ is in error due to its solubility in the coal. We disagree with this. The solubility of CO₂ in coals is not great enough to explain the large surface areas observed and CO₂ surface areas agree well with those obtained using X-ray scattering.^{1,9} It seems likely that the CO₂ surface areas are approximately correct for coals and we must seek an explanation for the anomalously low surface area obtained with cyclopropane.

If the CO₂ surface areas are approximately correct, then CO₂ must be able to reach coal surface which is inaccessible to cyclopropane. This brings us to consider the solubility of the two gases in coals. The solubility of CO₂ in coals has been experimentally demonstrated (see however ref. 10).⁷ Cyclopropane is probably insoluble in the coal. It has been established that alkanes do not swell coals to any appreciable extent and the heats of wetting of coals by alkanes is zero.^{11,12} We conclude that cyclopropane is probably insoluble in the coal.

This solubility difference is the basis of an explanation of the different surface areas obtained with these two gases. If a large portion of the pores in coals are closed, they will remain inaccessible to molecules unable to dissolve in coals. The pores are not directly connected to the external surface so a molecule must dissolve in and diffuse through solid coal to reach the closed pores. Adsorbate gases capable of dissolving the coal have accessibility to pores that are closed to insoluble molecules. Thus, soluble CO₂ gains access to all of the pores in this coal while insoluble cyclopropane can only reach those connected to the exterior by the pore network. If this is correct, most of the coal pore system is closed.

It can be argued that the coal is shape selective and that the rod-like CO₂ molecule can penetrate the pores while the flat

cyclopropane cannot. Work with amines has shown that planar molecules easily penetrate coals while branched molecules do not.¹³ It has been shown that both n-butane and CF_2Cl_2 also give low coal surface areas.^{14,15} If coals are shape selective, they are extraordinarily discriminating. Molecules such as methanol which interact specifically with coals and dissolve in them report very large surface areas which are incorrect.¹⁵ What is being measured is solubility in the coal, not surface area. It seems to us most reasonable to conclude that coal pores are mostly closed and inaccessible to molecules not soluble in the coal.

With this model there are three classes of sorbed molecules. Molecules which interact specifically and strongly with coals or which are soluble in coals report very large and meaningless surface areas. The experiment measures their solubility in the coal. Molecules which are insoluble in coals can be used to measure that part of the surface area which is open to the surface and accessible to the probe molecule. This accessibility is governed by the pore size, the molecule size, and the temperature since diffusion may be activated. Finally, there are those molecules whose solubility in coal is low, but which can penetrate all of coal by virtue of that solubility. These molecules will have access to all of the pores, even those not connected directly to the surface, and can be used to determine an approximately correct total surface areas.

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Table I. Surface Areas of Ill. #6 Coal

Adsorbate	Adsorption Temperature (°K)	Cross-Sectional Area (Å ²)	BET Surface Area (m ² /g)
Argon	77	16.2	14
			15
Carbon Dioxide	178	25.3	132
			132
Cyclopropane	203	25.2	36
			31

Table II. Surface Areas of Kentucky #12 (from ref.2)

Adsorbate	Cross-Sectional Area (Å ²)	BET Surface Area (m ² /g)
Nitrogen (77.8°K)	16.27	4
Carbon Dioxide	25.30	101

FIGURE I.

Dependence of Surface Area for Kentucky #12 Coal on Solvent Swelling (data from ref.2)

