

Pore Structure in Coals

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Received February 9, 1993. Revised Manuscript Received March 25, 1993

Attempts have been made for many years to delineate the pore structure and surface area of coals by measuring their uptake of gases, vapors, and liquids. Many of these studies have been conducted in our laboratory.¹⁻³ Although values determined for pore volumes and surface areas may vary markedly depending upon the sorbate used and conditions selected for uptake measurements, it is now generally agreed that coals possess a range of pore sizes—macropores (>20 nm), transitional pores (2–20 nm), and micropores (<2 nm).⁴ Coals of most ranks can be described as highly crosslinked and entangled networks of macromolecular chains of irregular structure. It is, therefore, not surprising that micropores are created as a result of the poor packing of these macromolecular chains.^{5,6}

It has long been recognized that when coals are exposed to sorbates, they swell, more or less. Whereas some swelling can be caused by adsorption of a liquid-like layer on the surface of pores,⁷ it is thought that imbibition of the sorbate into the solid structure of the coal is responsible for the majority of the swelling in most cases.⁸ The question then arises as to the primary way the sorbate reaches the microporosity in coal, that is, via the pore system of the coal or through the solid coal structure as a result of imbibing.

Larsen and co-workers have been interested in this question for some time.⁹⁻¹² Noting the low surface area

of coal as measured by inverse gas chromatography¹² and the unrealistically high fractal dimensionality of coal (23.5) determined upon exposing the coal to different sorbates,^{10,11} they conclude that “pores in coal are isolated from each other and can only be reached by diffusion through the solid, glassy macromolecular coal”. Further they conclude that “coals do not contain interconnected pore networks”. They say their conclusion that coals lack any interconnected pore network is consistent with their finding that molecules of closely similar shapes and diameters give very different values for coal surface areas. They cite the cases of ethane and CO₂, which have cylindrical shapes and only differ in diameters by 16%. They say that “diffusion through constricted openings cannot be responsible for this size discrimination”.

Consider evidence which contradicts the above conclusions of Larsen and co-workers. If all of the pore networks in coals were non-interconnected, their particle densities (as measured by Hg displacement) would equal their He densities (as measured by He displacement) since He imbibes to a negligible extent in coals.⁸ Such is not the case. In fact, for coals of all rank, He densities (ρ_{He}) are significantly higher than Hg densities (ρ_{Hg}).³ Specific pore volumes (V) open to He can be calculated from

$$V = \frac{1}{\rho_{\text{Hg}}} - \frac{1}{\rho_{\text{He}}} \quad (1)$$

Pore volumes in American coals of rank ranging from anthracite to lignite, accessible to He, vary from a low of about 0.02 to a high of 0.25 cm³ g⁻¹.^{3,4} Open porosities range from about 2% to 28%.

Many workers have shown that sharp size discrimination (sieving) of molecules exists in solids possessing pores of molecular diameters. This discrimination occurs in spite of negligible imbibing of the molecules by the solids. For example, 5A zeolites with aperture openings of 0.42 nm¹³ exhibit sharp differences in uptake of *n*-butane (0.131 g g⁻¹) and isobutane (0.005 g g⁻¹) at 298 K, despite the fact that *n*-butane has a minimum diameter only 14% smaller

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than that of isobutane.¹⁴ This discrimination is a result of activated diffusion through the apertures, with *n*-butane having a significantly lower activation energy for diffusion than does isobutane. Consider another example—CO₂ (kinetic diameter $\sigma = 0.33$ nm) and N₂ ($\sigma = 0.36$ nm) in the 3A zeolite. In spite of the σ for N₂ being only 9% larger than that for CO₂, the activation energy for the diffusion of N₂ is 68 kJ mol⁻¹ compared to only 18 kJ mol⁻¹ for CO₂.¹⁴ At 298 K, the ratio of the values for diffusion coefficients for CO₂ and N₂ is about 10³. Finally, commercial separation of O₂ from N₂ on carbon molecular sieves is practiced¹⁵ even though the σ for N₂ (0.364 nm) is only about 5% larger than the σ for O₂ (0.346 nm). At 298 K, the ratio of the values for diffusion parameters for O₂ and N₂ in a commercial carbon molecular sieve is about 32.¹⁶ Again imbibition of the sorbate is negligible for this system.

In conclusion, the fact that molecules of similar dimensions give very different coal surface areas does not necessarily mean that access of these molecules to the

microporosity in coal occurs solely by diffusion through the solid coal. It could also be attributed to diffusion through the pore system. The extent to which access to the micropore system can be attributed to diffusion through the solid coal as compared to diffusion through the pores depends upon the molecule undergoing diffusion. At the one extreme will be He where diffusion through the pore system accounts for essentially all the mass transport. At the other extreme will be larger organic molecules having solubility parameters closely matching those of the coal.¹⁷ In this case essentially all of the access to the microporosity in coal is a result of imbibing and diffusion through the solid phase. In such cases considerable swelling of the coal occurs.

In any case, utilization of the high surface area found in the micropores of coals in important reactions involving coal is poor, because of activated diffusion of reactants and products either through the pore system or through the solid coal. This is the main point which Larsen and co-workers wanted to make and for which they deserve credit.

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