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ABSTRACT

Known O-alkylation procedures have been used to derivatize the carboxyl and hydroxyl groups in the APCS coals Lewiston-Stockton, Wyodak-Anderson, Beulah-Zap, Illinois #6, Upper Freeport, and Pittsburgh #8. In general the resulting decrease in hydrogen bonding reduced the cyclical variation in nitroxide spin probe retention observed for nonalkylated coals when small amounts (<1%) of pyridine are present in the toluene swelling solvent. An increase in spin probe retention by the O-alkylated coals relative to the underivatized coals indicates a more open arrangement in the coal due to a decrease in attractive forces, confirming that microporosity increases with increasing rank.

INTRODUCTION

A recent study of Tucker,¹ using an EPR spin probe method we have developed, and an earlier study by Green and Larsen² showed that an unexpectedly large number of guest molecules could be included in the swelled macromolecular structure of coal by spiking a "poor" swelling solvent such as toluene (or chlorobenzene) with as little as 100 ppm of a strong swelling solvent such as pyridine. The specific amount of included guest material depends on the rank of the coal undergoing swelling, but all ranks showed reproducible fluctuations in the number of trapped guest molecules as the pyridine content was increased by increments of 100 ppm. This oscillatory uptake behavior was explained as follows. At low ppm pyridine, weak hydrogen bonds which isolate interconnected micropore systems are disrupted. As the concentration of pyridine increases, disruption of weak hydrogen bonds which protect individual micropores will occur, followed at 1-5% pyridine by disruption of stronger hydrogen bonds within the macromolecular structure resulting in an opening of the structure. The cartoon given in Figure 1 emphasizes the active sites that can hydrogen bond (OH) with guest molecules, the interconnected micropore system, the hydrogen bonds of individual micropores and the stronger hydrogen bonds within the macromolecular structure.

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SWELLING BEHAVIOR OF O-ALKYLATED APCS COALS
AS EXAMINED BY THE EPR SPIN PROBE METHOD
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KEYWORDS: O-Alkylated Coal, EPR Spin Probe, Hydrogen Bonding

New Analytical Methods for Characterizing
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Direct Coal Liquefaction
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Electron paramagnetic resonance (EPR) techniques have been used previously to follow the inclusion of molecular probes in the micropore structure of coal in order to determine the changes in pore size, shape characteristics, pore wall chemistry, and hydrogen bonding which occur during the swelling process.⁶

The most common molecular probes are stable cyclic nitroxyl free radicals (depicted in Figure 2) which contain a ring nitrogen that is also singly bonded to oxygen and flanked by four methyl groups which sterically stabilize the radical. The unpaired electron density is distributed over both the nitrogen (40%) and the oxygen (60%) atoms. Reactive substituents (R) on the ring allow for chemical reactions to be studied, and varying the size and shape of a non-reactive substituent, allows evaluation of the effect on shape or size of the structural features of coal. The spin probe technique has been described in detail.⁶ Briefly the coal sample is swelled in a mM nitroxide spin probe solution for approximately 18 h until equilibrium is reached. The coal slurry is then filtered and the solid is vacuum dried to remove the swelling solvent. The samples are then washed with cyclohexane, a non-swelling solvent, to remove any spin probes not trapped in the coal structure. The samples are again vacuum dried and then sealed in evacuated EPR tubes for subsequent measurement of the concentration of the nitroxide radicals trapped in the coal structure.

EXPERIMENTAL

Spin probe VII (Tempamine) was obtained from Aldrich and used as received. This probe contains an amino group which can react with acidic sites in the coal, or in the absence of such sites, it can be trapped in small pores. Ca. 4 g of APCS coal samples, obtained from the Argonne Premium Coal Sample program,^{3,4} were O-alkylated according to a literature method,⁵ although the work-up procedure was modified as follows. Warm water (100 mL) was added to the reaction mixture and the pH was adjusted to 7. Volatiles were removed by distillation under vacuum for 2 h at 22 °C and then at 40 °C for 3 h. The residue was treated with hot water (500 mL) to dissolve ammonium salts. The mixture was left to stand overnight; the aqueous layer was decanted, and the procedure was repeated 5 times. The product was isolated by filtration and washed with hot water (4-6 L) until the washings were devoid of halide ions. The alkylated coal was first dried over CaCl_2 under N_2 , then under vacuum for 2 days and finally at 110 °C for 3 days. The alkylated coal was sealed under N_2 . Infrared analysis was used to follow the decrease in adsorption in the 3300-3600 cm^{-1} region (loss of hydroxyl groups) and the adsorption increase in the 1730 cm^{-1} region (esterification of the carboxylic acids).

RESULTS AND DISCUSSION

The retention of spin probe VII in BZ APCS lignite is given in Figure 3 as a function of percent pyridine present in toluene swelling solvent. The important feature to note is that large variations occur in the spin probe retention. In the absence of pyridine 1.2 $\times 10^{18}$ spins/g of probe VII is retained in the BZ lignite. When very small amounts of pyridine are present the spin probe retention drops to 0.8 $\times 10^{18}$ and then increases to 1.8 $\times 10^{18}$ with 0.1% pyridine. A decreasing variation in the amount of spin probe retained occurs as the percent pyridine in toluene is increased, becoming more or less constant near 0.4 $\times 10^{18}$ spins/g.

Totally different behavior, shown in Figure 4, of spin probe VII retention as the percent pyridine is increased occurs with O-alkylated BZ. The highest spin probe retention (4.1 $\times 10^{18}$ spins/g) is obtained in the absence of pyridine and this then decreases without any evidence of oscillation to ca. 2.4 $\times 10^{18}$ spins/g with a pyridine content of $\geq 0.5\%$.

Similar plots for Wyodak-Anderson coal and alkylated Wyodak-Anderson coal are given in Figures 5 and 6, respectively. As the percent pyridine increases from 0% to 0.01% (Figure 5) the retained spin probe concentration in units of 10^{18} spins/g drops from 6.1 to 4.8, then rises to 5.5 at 0.02%, drops to 3.6 at 0.08%, rises to 4.9 at 0.1%, drops to 3.2 at 0.2%, rises to 5.5 at 0.6%, and drops to 3.1 at 1%. Further variation is observed as the pyridine content increases to 5%. Above 5% the retained spin concentration equals approximately 3.7 \pm 5. For the alkylated coal (Figure 6), the spin concentration is nearly constant at $9.0 \pm 0.2 \times 10^{18}$ spins/g with the variation close to the relative error of ± 0.1 .

Figures 7 and 8 show the results of a similar study for Lewiston-Stockton and alkylated Lewiston-Stockton coal, respectively. The spin probe concentration in units of 10^{18} spin/g (Figure 7) varies from 2.2 at 0% pyridine to 1.8 at 0.06%, increases to 2.1 at 0.08%, decreases to 1.7 at 0.4%, increases to 2.0 at 0.6%, and then decreases to 1.6 at 1%, 1.4 at 2% and 1.2 at 4%. In contrast, the spin probe retention in the alkylated coal (Figure 8) decreases from 7.6 at 0% pyridine to 6.9 at 0.2% and then gradually increases to 7.4 at 2%.

In all three coals, the absolute value of the spin probe concentration increased upon alkylation (a factor of 4 for Beulah-Zap, lignite; 2.5 for Wyodak-Anderson subbituminous and 5.4 for Lewiston-Stockton high volatile bituminous coal). Previous porosity measurements⁵ indicated that an increase in microporosity occurs upon alkylation and that this increase is more pronounced in high ranked coals than in the lower ranked coal. This is confirmed by this study. It is also clear that upon alkylation the cyclical variation is nearly eliminated, confirming the role of the hydrogen-bonding scheme outlined in the introduction. The largest variation in spin concentration with % pyridine occurred for Wyodak-Anderson coal suggesting more extensive changes in local structure with pyridine at less than 1% than for the high ranked Lewiston-Stockton coal. Beulah-Zap, which loses water upon exposure to air, has a lower tendency to retain the spin probe than the high rank Lewiston-Stockton coal.

ACKNOWLEDGMENT

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Figure 1

A cartoon depicting a possible pore structure with the location of (OH) sites that can hydrogen bond with guest molecules and localized hydrogen bonding (---).

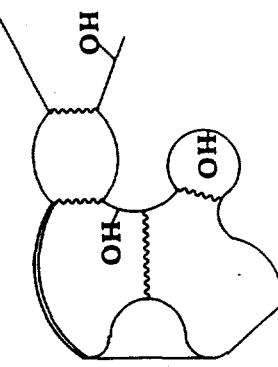


Figure 2

(a) General structure of a nitroxide spin probe,
 (b) Structure of spin probe VII (TEMPAMINE)

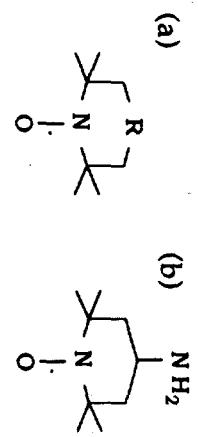


Figure 5
 Retention of spin probe VII in Wyodak-Anderson sub-bituminous APCS coal after swelling with toluene spiked with pyridine.

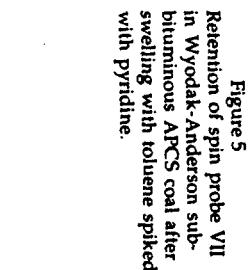


Figure 3
 Retention of spin probe VII in Beulah-Zap APCS lignite after swelling with toluene spiked with pyridine.

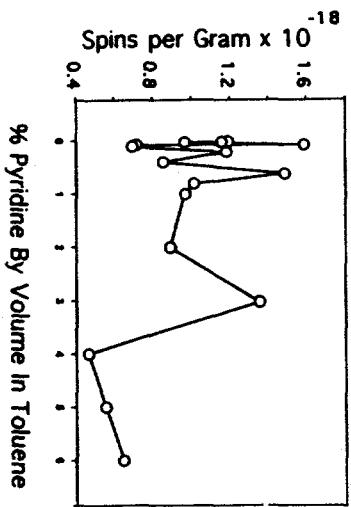


Figure 6
 Same as Figure 5 except with O-alkylated Wyodak-Anderson coal.

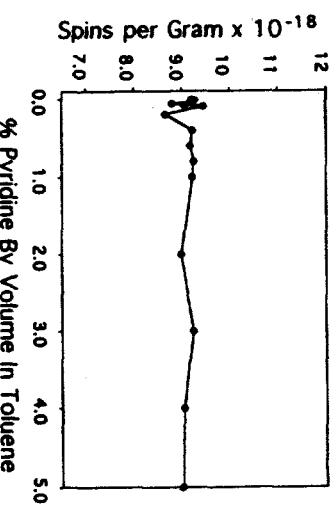


Figure 7
 Same as Figure 5 except with Lewiston-Stockton high volatile bituminous APCS coal.

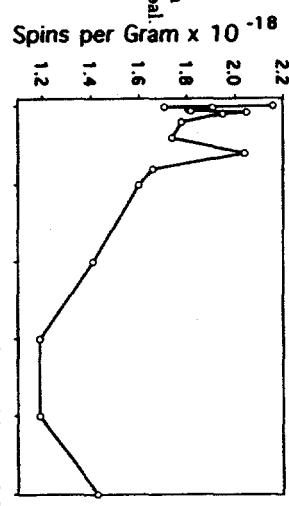


Figure 4
 Retention of spin probe VII in O-alkylated Beulah-Zap APCS lignite after swelling with toluene spiked with pyridine.

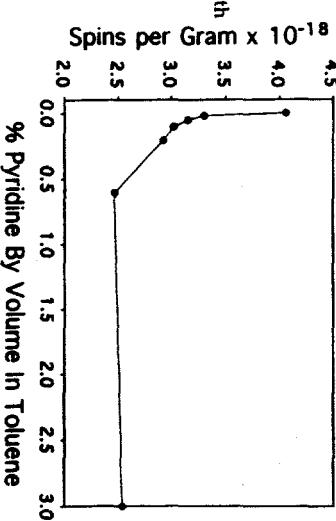
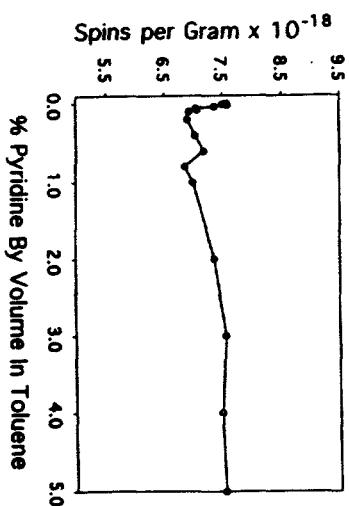


Figure 8
 Same as Figure 5 except with O-alkylated Lewiston-Stockton coal.



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