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AN EPR SPIN PROBE METHOD FOR CHARACTERIZING CHANGES IN THE ACCESSIBLE REGIONS OF COAL UPON OXIDATION

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ABSTRACT

Eight Argonne Premium Coal Samples (APCS) were weathered in air and the structural and chemical changes that occurred upon swelling with toluene and pyridine were examined by an EPR spin probe method developed in this laboratory. Under mild oxidation conditions and swelling with toluene large structural changes were observed for lignite (Beulah-Zap) which suggested the collapse of the coal structure. This did not occur for higher rank coal. Upon oxidation and swelling with toluene and pyridine an increase occurred in the amino substituted spin probe concentration for coals with the carbon percent above 80%. A maximum was found for the creation of 5 Å diameter pores upon swelling with pyridine at 85% C.

INTRODUCTION

The conversion of coal by an economically feasible catalytic method is an area of research for our future energy requirements. However, knowledge of the coal structure (1, 2) is necessary before optimum use of a catalyst can be made. For instance, in addition to the normal surface catalysis, the catalyst must be able to diffuse into the coal, enabling catalysis to occur from within. This requires knowledge of the pore molecular accessibility size and shape in the coal. Any conversion process, however, involves exposure of the pore structure to solvents of various polarity, temperature and pressure variation, and catalytic action. Complicating the process can be oxidation processes that occurred before the coal is processed.

Oxidation (3) is of the utmost importance in many respects. Autogenous heating in a coal stockpile causes oxidation and even combustion of coal. In either case, sever detrimental changes to coal properties occur. Oxidation affects thermal and swelling properties which are important in coke production. Oxidation also affects solvent swelling properties, important in catalytic conversion.

However, the oxidation process is difficult to study, quantitatively or qualitatively. The amount of oxygen has been determined by neutron activation analysis (4) and by XPS analysis of the coal surface (5,6). Relative changes in the properties of the coal have also been used to measure oxidation. These include FTIR signatures, (7) pH, (8) Gieseler fluidity, (9,10) pyrolysis response, (11, 12) and free swelling index (13). In spite of these advance techniques, it is difficult to quantify the low temperature oxidation, as the amount of solid oxidation products are small (14). XPS measurements in conjunction with GC analysis of the gas products and thermal gravimetric analysis (GA) of the fuels (15) can be useful in determining the oxidation process.

In addition, drying of the coal results in pore collapse which changes the mechanical properties (1, 2) so the coal becomes more friable. Reswelling the dried coal is believed (1, 2) to cause autogenous heating of the coal.

The micropore structure of coal has been characterized by both sorptive methods (16-18) and spectroscopic methods. The spectroscopic methods have included small-angle X-ray (SAXS)

(19) and neutron (SANS) (20-22) scattering where micropores can be observed in the presence of solvent molecules. Low field NMR spin lattice relaxation measurements (23, 24) of the water in the pores of the coal enabled a study of pore radius from <0.5 mm to 0.5 mm.

EPR spin probe studies in the absence of oxidation

Previous electron paramagnetic resonance (EPR) spin probe (25-30) studies of APCS samples have dealt with the effect of swelling temperature, micropore size and shape, solvent polarity, spin probe imbibition, and polarity of the spin probes. The results of these studies have correlated well with SANS (19), SAXS (20-22) and NMR (23, 24) studies of APCS coals upon coal swelling.

It was observed by the EPR spin probe method that APCS samples swelled at 298 K in toluene did not changed the micropore structure in any significant way (29). It was found (28, 29) that coals swelled in toluene contained small, spherically shaped pores and a broad distribution of cylindrical shaped pores of short length. Elevating the swelling temperature from 298 K to 333 K had no effect on nonpolar solvents (toluene), only a mild effect on slightly polar solvents (nitrobenzene) and a significant affect on very polar swelling solvents (pyridine).

Polar solvents caused elongation of the micropores (29). The greater the swelling temperature and the greater the swelling solvent polarity, the greater the degree of micropore elongation. Nitrobenzene at 298 K showed only small micropore elongation. However, small spherical pores did disappear entirely. At 333 K in nitrobenzene, significant pore elongation did occur, with the creation of a bimodal pore size distribution. Coals swelled in pyridine at 298 K exhibited significant pore elongation, and the creation of a bimodal pore size distribution. Elevation of the swelling temperature to 333 K caused much greater micropore elongation. This bimodality was confirmed through the use of alkylammonium spin probes, which behaved more like nonpolar spin probes than as cationic moieties.

The effect of solvent polarity was found to be related to the types of cross-linking in coal. Toluene did not disrupt either covalent or noncovalent linkages and so did not swell coal significantly under these conditions. Polar solvents like nitrobenzene and pyridine swelled coal by disrupting hydrogen bonds. A solvent which was more polar (i.e., had a greater hydrogen bond accepting ability) could disrupt more bonds and swell coal to greater degree. More polar solvents took longer to reach swelling equilibrium. Increasing the swelling temperature had the effect of hastening the approach to equilibrium and so caused greater pore swelling and elongation.

Micropore elongation was ascribed to swelling anisotropy in coal. It was determined that most of the micropore elongation took place parallel to the bedding plane. This led to the development of a "zipper" model for coal swelling (29).

Rank effects was shown to be an important factor in spin probe imbibition (29). Coals at 85% carbon (dmmf) and above typically showed similar spin probe retention curves. Spin probe concentration, where significant retention occurred, decreased with rank. The retention curves showed a minimum in the range 85-92% carbon (dmmf). For coals swelled in toluene, the minimum was directly related to a minimum in porosity in this range.

For coals swelled in polar solvents, the decrease in spin probe concentration was associated with rank, and the increase in covalent cross-links. The decrease in hydrogen bond cross-link density in APCS coals was in turn associated with the decrease in oxygen functionality concentration, especially hydroxyl content, with rank.

Spin probes with polar R groups showed selective retention over nonpolar spin probes of same size. Spin probe retention was dependent on the polarity of the R group, which proceeded in the order -H << -OH < $-CO_2H$ < NH_2. Spin probe retention for moderately polar spin probes increased with swelling temperature for coals swelled in toluene. This increase was ascribed to hydrogen bond disruption by the spin probes. The most polar spin probe (R = $-NH_2$) showed no temperature effects up to 333 K, apparently because its R group was strong enough to cause significant hydrogen bond disruption.

Varying the swelling solvent polarity resulted in a competition of the solvent molecules with the polar spin probes for hydrogen bonding sites. Raising the swelling temperature resulted in increased solvent competition for hydrogen bonding sites. The effect of temperature was significantly greater as solvent polarity increased.

It was shown that "acidity" and "basicity" were incorrect terms in considering coal micropore wall chemistry. The terms "hydrogen bond donor" and "hydrogen bond acceptor" were used instead. Polar spin probes interacted with coal primarily as hydrogen bond acceptors. Acidic spin probes showed some indication of acting as hydrogen bond donors, but the primary mechanism of interaction was as an acceptor.

For coal swelled in polar solvents, the decrease in spin concentration was associated with the decrease in hydrogen bond-type cross-link concentration with rank, and the increase in covalent cross-links. The decrease in hydrogen bond cross-link density in APCS coals was in turn associated with the decrease in oxygen functionality concentration, especially hydroxyl content, with rank.

Recently, measurements of Argonne Premium Coal Samples (APCS) in our lab using the EPR spin probe technique that we developed suggests that the study of the oxidation processes and the change in structure upon drying can be followed by the EPR spin probe technique. This paper details the study of oxidizing coal for eight days and outlines additional experiments which lead to a further understanding of the oxidation process in the pore structures of coal.

EXPERIMENTAL

Ampoules containing all eight APCS coals were opened and their content was placed in a number of vials, 250 mg of coal in each vial. The vials with coals were weighted, and then placed on a shelf in room temperature and humidity about 60% protected from dust. The coals were stirred every day.

At the beginning samples from fresh coals were made, then samples were prepared from coals weathered for 8, 15, 36, 64 and 119 days. The vials with weathered coals were weighed, the values of the loss of weight after n days of weathering are given in Table 1.

Our standard procedure of imbibing spin probes into the pore structure of coals in the presence of swelling solvent was applied (28, 29). Coals were swelled in 60 °C for 18 hours in toluene or pyridine. Spin probes used were VI (3-carboxy-2,2,5,5-tetramethylpiperidine-1-oxyl), VII (TEMPAMINE, 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl), and VIII (TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl). All spin probes are spherically shaped and are similar in size, the difference between then is the polarity of the R group [Figure 1]. Spin probes I-X were previously defined (26).

EPR spectra of the spin probe doped coal samples were recorded. The method of computing the nitroxide radical spin probe concentration was described previously (26,27). The results of the first 8 days of oxidation are presented in Figures 2-4.

RESULTS AND DISCUSSION

The concentration of spin probe VI (carboxyl substitutent, polar group interactions) as a function of toluene and pyridine as the swelling solvent for APCS coal in the absence of air is given in Figure 2a. A general increase in the number of hydrogen bonding sites is observed as the rank decreases. It is known that the lignites contain more hydroxyl functional groups than the higher rank coals, thus the observed increase in the concentration of trapped spin probe VI for both solvents. The lower concentration of VI in pyridine is due to competition of pyridine for the polar sites, which does not occur in the case of toluene. Upon weathering the coal for 8 days in air (Figure 2b), a large decrease in the concentration of VI is observed for lignite (74-76% C) swelled in toluene. This can be explained by the data of Yost and Creasy (31) that the loss of water from the coal structure (which we also observed) collapses the structure, making it more difficult to trap the small spin probe VI in the coal structure unless the energy barrier can be overcome. A weight loss of 20-25% occurred for 74% C but none for 92% C (Table 1). However, the use of pyridine disrupts the collapsed coal structure so no difference is observed for pyridine solvent in the concentration of spin probe VI over the entire coal rank, while the same is true above 76% C when toluene is the swelling solvent. This observation suggests that we can follow changes in the hydrogen bond energy distribution. Further oxidation for 15 days shows an increase in spin probe concentration at 85% C content when toluene solvent is used indicating an increase in the formation of oxygen groups. This suggests that we can follow oxidation kinetics as well as changes in pore shape and size.

The biggest effect upon weathering in an oxygen atmosphere occurs when solutions of spin probe VII (NH_2 substituent) is slurried with the APCS coals. In the absence of air (Figure 3a) the concentration of VII is similar to VI using toluene as the swelling solvent but is larger for VII than VI when pyridine is the swelling solvent. However upon exposing the coal for 8 days to air a dramatic increase occurs in the concentration of VII for both toluene and pyridine as the swelling solvent above 76% carbon (Figure 3b). Below 76% C, the collapse of the coal structure upon loss of water is observed when toluene is used preventing the trapping of VII. Use of pyridine as the swelling solvent opens up the collapsed structure, allowing the trapping of VII. Upon oxidation for 15 days, the concentration of spin probes VII in pyridine solvent continues to increase due to the interaction of the NH_2 group with the oxidized coal.

The concentration of a spin probe with no substitutent (VIII) and thus only size effects are studied, is depicted in Figure 4a. The concentration of VIII for both toluene and pyridine solvents is an order of magnitude or more lower for VIII than for VI and VII. Interestingly the concentration of VIII in toluene increases with decreasing rank while VIII in pyridine reaches a maximum at 86% C. These features can be rationalized by the opening of the coal structure by the pyridine – allowing all the spin probe concentrations to be washed out at low rank and the coal structure opened sufficiently in some places to trap VIII at 86% C. Upon weathering in air (Figure 4b), the concentration of VIII increases with the maximum still at 86% in a pyridine solvent while the loss of structure can be detected when swelled in a toluene solvent. Further oxidation for 3 weeks shows the maximum at 86% C – suggesting some interesting changes in the swelling characteristics as a function of oxidation. It is important to note that the concentration of VIII is very small but the polar VI and VII spin concentration is large. This observation indicates that even small degrees of oxidation can be detected.

CONCLUSION

The large decrease in the concentration of the spin probe after oxidation of lignite (74%) for eight days and swelled in toluene, appears to be due to the collapse of the coal structure upon oxidation as a result of water loss. However swelling with pyridine reopens the collapsed structure and no detectable difference is observed upon oxidation. For higher rank coal, a larger concentration of amino substituted spin probes was trapped upon swelling with toluene and pyridine after air oxdiation for 8 days. The decrease in amino substituted spin probe for fresh Beulah-Zap showed a measurable increase upon oxidation and swelling in pyridine. Swelling with pyridine opens up small pores for 81-86% which is not observed for swelling with toluene. Changes in coal structures due to oxidation can followed by the EPR spin probe method.

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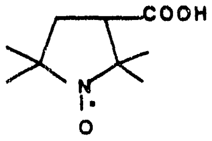
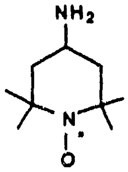
Table 1. Weight loss (% ± 0.4%) of APCS coals after n days of weathering.

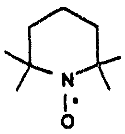
Coal	Carbon Content	days 8	15	36	64	114
Beulah-Zap	74.05%	21	25	23	23	25
Wyodak-Anderson	76.04%	19	20	20	21	21
Illinois #6	80.73%	4.5	5.5	5.5	5	5.3
Blind Canyon	81.32%	1.2	2	1.5	1.6	1.2
Pittsburgh #8	84.95%	0	0	0.2	0.4	1.2
Lewiston-Stockton	85.47%	0.8	1	1	1.4	1
Upper Freeport	88.08%	0.6	0.8	1	1	0.6
Pocahontas	91.81%	0	0	0	0	0



VI



VII



VIII

Figure 1. Spin probes VI, VII, and VIII.

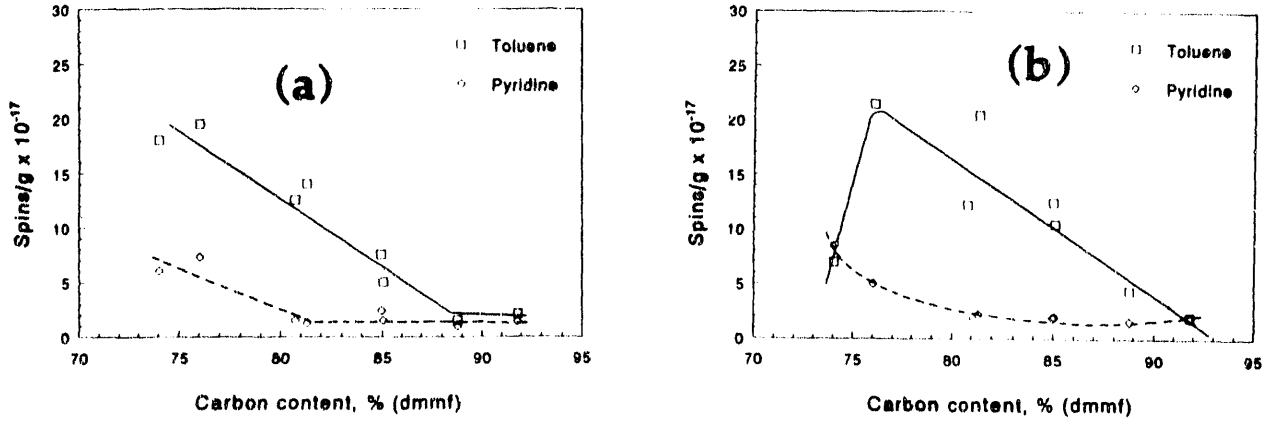


Figure 2. Concentration of spin probe VI versus percent carbon content (dmmf) in APCS coal swelled at 60 °C in toluene (□) and in pyridine (♦), (a) as received and (b) after weathered for 8 days in air at room temperature.

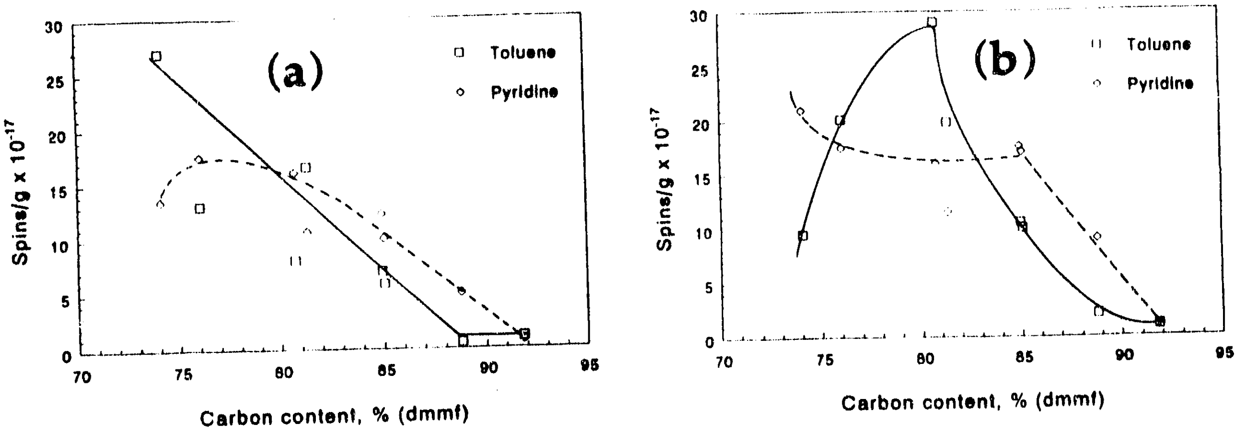


Figure 3. Spin probe VII versus percent carbon content (dmmf) in APCS coal swelled at 60 °C in toluene (□) and in pyridine (♦), (a) as received and (b) after weathered for 8 days in air at room temperature.

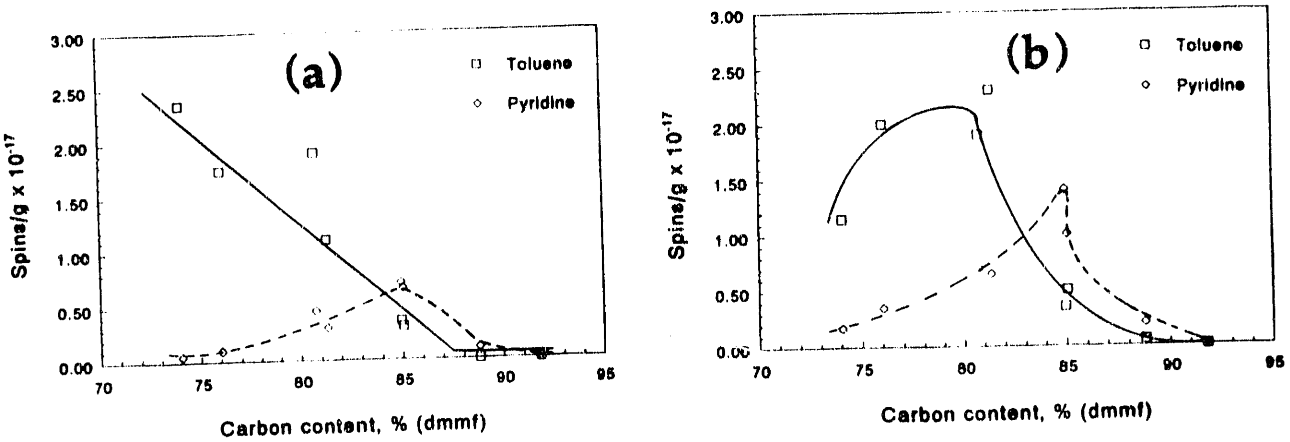


Figure 4. Spin probe VIII versus percent carbon content (dmmf) in APCS coal swelled at 60 °C in toluene (□) and in pyridine (♦), (a) as received and (b) after weathered for 8 days in air at room temperature.

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