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Resolution Test Chart Labels:

- 1.0
- 1.1
- 1.25
- 1.4
- 1.6
- 1.8
- 2.0
- 2.2
- 2.5
- 2.8
- 3.2
- 3.6
- 4.0

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Molecular Accessibility in Solvent Swelled Coals

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EXECUTIVE SUMMARY:

The conversion of coal by an economically feasible catalytic method requires the catalyst to diffuse into the coal sample so that hydrogenation catalysis can occur from within as well as the normal surface catalysis. Thus an estimate of the size, shape, and reactivity, of the pores in the coal before and after the swelling with different solvents is needed so that an optimum sized catalyst will be used. This study characterizes the accessible area found in Argonne Premium Coal Samples (APCS) using a EPR spin probe technique. The properties deduced in this manner correlate well with the findings deduced from SANS, NMR, SEM, SAXS and light scattering measurements.

PROJECT SUMMARY:

The use of nitroxide spin probes with swelling solvents is a simple way in which to gain an understanding of the pore structure of coals, how it changes in the presence of swelling solvents and the chemistry that occurs at the pore wall. Hydrogen bonding sites occur primarily in low-rank coals and vary in reactive strength as rank is varied. Unswelled coals contain small, spherical pores which disappear when coal is swelled in the presence of polar solvents. Swelling studies of polystyrene-divinyl benzene copolymers implied that coal is polymeric, contains significant quantities of covalent cross-links and the covalent cross-link density increases with rank.

RESEARCH WORK COMPLETED:

An EPR technique developed in this lab¹⁻³ has been used to determine the pore size and number distribution changes after swelling the coal samples with various solvents. Stable nitroxide radical spin probes of different sizes, shapes and reactivity are dissolved in an appropriate solvent, the coal sample is then added to the

resulting solution, stirred overnight at elevated temperature, filtered, washed with a non swelling solvent to eliminate any spin probes that are not trapped in the pores and the spin concentration is measured. Comparing these spin probe measurements to DRIFT data have shown⁴ that the relative number distribution of acidic functionalities can be accurately predicted by the spin probe method. The spin probe method has also been used to predict⁴⁻⁵ the increase in elongated voids in Pittsburgh No. 8 (APCS No. 4) upon swelling with pyridine in agreement with independent SANS data. NMR relaxation data show³ that it is possible to deduce the pore (accessibility) distribution as a function of size (up to 6 nm). It has also been possible by variable temperature¹⁻³ and ENDOR measurements⁶ to determine the presence of hydrogen bonding as a function of pore shape and size. The advantage of the EPR method is that it permits molecules of selected shape, size and reactivity to be used as probes of accessible regions of coal, thus providing information of importance to the diffusion and reactivity behavior of catalysts in coal.

To expand the information base on molecular accessibility in solvent swelled coal, Argonne Premium Coal Samples (APCS) were swelled in polar, basic solvents before and after moisture loss and upon air oxidation. So far studies have been reported^{7,8} on the changes in pore size distribution as a function of temperature when polar basic swelling solvents are used. Additional studies employing EPR spin probe techniques performed on the breaking up of the hydrogen bonding between bedding planes^{9,10} were later confirmed by magnetic resonance imaging at Argonne National Lab and the University of Illinois.

A paper¹¹ that we have recently published in the journal, *Fuel* detailed the behavior of APCS micropore wall chemistry during swelling. Studies of spin probe retention with increasing spin probe polarity, provided valuable insight into the hydrogen bond cross-link density and oxygen functionality of APCS coals.

Eight Argonne Premium Coal Samples (APCS) were weathered in air for 8 days and the structural and chemical changes that occurred upon swelling with toluene and pyridine were examined by our EPR spin probe method. The large structural changes were attributed to collapse of the coal structure. The results were reported¹² at the ACS Fuel Chemistry Division Annual meeting in Washington, DC, August 23-26, 1992 in the Symposium on Analytical Techniques for Characterizing Coal and Coal Conversion Products.

The EPR spin probe technique was used to examine the swelling behavior of 2% to 12% cross-linked polystyrene-divinylbenzene (PSDVB) copolymers to gain insight into the molecular accessibility of covalently cross-linked coal. Since these copolymers can be highly cross-linked with covalent interactions, without the presence of hydrogen bonding or other polar interaction prominent in coal, they are valuable models for studying the molecular accessibility as a function of only the covalently cross-linked character in coal.

Because the polymers contained no polar functional groups, selective retention of I, TEMPO (R = OH, a spherical molecule with a hydrogen bond site) over VIII, TEMPO (R = H, a spherical molecule with no hydrogen bonding site) was not observed. Pyridine was determined to be a much better swelling solvent than toluene for PSDVB, however, toluene was shown to be a much more effective solvent for the inclusion of spin probes in the macromolecular structure of PSDVB copolymers following a cyclohexane wash. It was demonstrated that most of the spin probe retention was due to the intercalation of the guest molecules into the structure of the copolymers and not to any inclusion of spin probes in pre-existing pores accessible from the surface of the polymer beads. The extent of hydrogen bonding in coal was inferred to have a much greater impact on its swelling properties than its covalently cross-linked character. However, significant amounts of spin probe retention can be achieved in covalent cross-linked materials.¹³

The effect of weathering (oxidation and dehydration upon exposure to air) on the molecular accessibility of potential catalysts was studied by the EPR spin probe technique. Fresh samples of all 8 APCS coals were exposed to air for periods up to 36 days. Weathering produced significant effects on the retention of spin probes in most of the APCS coals under 91% carbon (dmmf). It was determined that the lower ranked coal (Beulah Zap and Wyodak) underwent a structural collapse which precluded retention of even spin probe VIII. However, medium ranked coals exhibited improved retention upon weathering when swelled in toluene. Swelling with pyridine opened up small pores for 81% - 86% carbon which is not observed for swelling with toluene. Changes in coal structure were successfully followed by the EPR spin probe method.¹⁴

A detailed analysis of the data collected from the swelling of coals oxidized in a moisture free environment was completed to differentiate between weathering and oxidation. Eight vacuum dried APCS coals were oxidized in an enclosed, pure oxygen, moisture free environment, and the effects of oxidation alone on coal structure were studied by the intercalation of EPR spin probes. The data shows a factor of 5 increase in spin probe retention for some coals oxidized in O₂ versus air, suggesting a large increase in oxidized material. Particular care was taken during the swelling procedures to avoid exposure of the coal samples to air or moisture. EPR spectra were then obtained for these 300 samples.¹⁵

The effects of short term exposure of Illinois #6 swelled in toluene to both argon and oxygen on the retention of spin probe VI were examined. It is clear from these studies that significant structural changes in Illinois #6 can occur in as little as 30 seconds of exposure to a dry gas environment. This suggests that the design of an experiment to study coal properties must consider the effect of a drying and oxidizing atmosphere.¹⁶

CONCLUSION:

The EPR spin probe method has provided valuable insight into the micropore size and shape characteristics of the APCS coals during the swelling process. This technique also proved to be sensitive to changes in the coal structure brought about by variations in swelling solvent polarity, swelling temperature and other modifications of experimental conditions during the swelling process. Successive experiments showed that monitoring the accessibility of spin probes to the pore structure of coal could be used to follow the physical and chemical changes in coal during weathering. This is being studied in detail by another funded program.

RECOMMENDATION:

Changes in coal structures on the molecular level can be detected by the EPR spin-probe technique. This method provides valuable insight into chemical reactions that occur or that can be carried out in coal. The method complements other measurements such as SANS, SAXS, NMR, SEM and imaging techniques with the added advantage that selected chemical reactions can be studied in an otherwise heterogeneous material like coal. Substantial advances in the knowledge of the chemical reactions, porous structure and the swelling process has been deduced by this study.

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PUBLICATIONS RESULTING FROM THIS GRANT:

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Attached to this FINAL REPORT are copies of the published papers. These are reference numbers 8-16.

STUDENT AND DEGREE RECEIVED:

Dennis Ross Spears, Ph.D. "The Effect of Low Temperature Swelling on the Micropore Structure of Coal and Model Polymers as Determined with a Novel EPR-Spin Probe Method," University of Alabama.

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