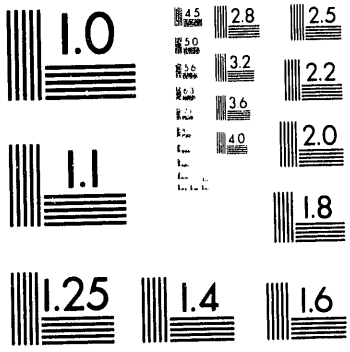
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# Molecular Accessibility in Solvent Swelled Coals

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## PREVIOUS WORK COMPLETED

An EPR technique developed in this lab[1-3] 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 over night 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 shown[4] that the relative number distribution of acidic functionalities can be accurately predicted by the spin probe method. The spin probe method had also been used to predict[4-5] the increase in elongated voids in Pittsburgh No. 98 (APCS No. 4) upon swelling with pyridine in agreement with independent SANS data. NMR relaxation data show[3] 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 temperature[1-3] and ENDOR measurements[6] 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 braking 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 paper[11] has just appeared in the Journal, *Fuel* on the 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. A copy of the reprint is attached.

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 reported[12] 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 interactions 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, TEMPOL (R = OH, a spherical molecule with a hydrogen bond site) over VIII TEMPOL (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) under went 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 $O_2$ 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]

## SUMMARY OF CURRENT ACTIVITIES

This quarter, three papers[14-16] were published in the *American Chemical Society Fuel Chem. Prepr.* and one paper was accepted for publication in *Energy and Fuels*.[13] Two talks were given by the P. I. and one talk by graduate student David Tucker at the 206th ACS Nation Meeting held in Chicago, Illinois, August 22-26, 1993.

David Tucker was also invited to present our work with the EPR spin probe method on determining molecular accessibility in coal as a function of swelling solvent, and temperature as well as his extensive work on wood pyrolysis and flash pyrolysis of biomass at the conference on the Production of Energy in Tanzania, June 1-8, 1993 held in Dar Es Salaam, Tanzania, Africa. His expenses were entirely bore by the Ministry of Water, Energy and Minerals of the United Republic of Tanzania. Tutorial lectures were presented by David in Swahili to Tanzanian' students form June 7 to June 11. David is fluent in Swahili learned when he spent some time in Africa in the early 1980's.

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 this quarter. Dramatic effects are seen on the retention of spin probe VI after just 30 seconds. After 30 seconds, a decrease of over 1200 x $10^{15}$ spins per gram is observed for coal exposed to argon. The decrease in retention is somewhat less pronounced for exposure to oxygen. After 5 minutes of exposure to argon, the retention characteristic of Illinois #6 returned to that found for fresh coal. The increase for oxygen followed the same trend, but to a far less extent. At 5 minutes, the difference between dehydrated (argon only) and oxidized coal is significant. This difference becomes more pronounced after 50 minutes of exposure. In the first 5 minutes, oxidation seems to cause changes which counteract the effects of dehydration. Beyond 30 seconds, oxidation caused a decrease in the retention of spin probe VI,

indicated by the increasing retention difference with exposure to oxygen as compared with argon. At 5 minutes or more, dehydrated coals (argon) have a much higher retention of spin probe VI than dehydrated and oxidized coal. Similar studies were also carried out with spin probe VII and VIII.

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]

## STUDIES PLANNED FOR NEXT QUARTER

This next quarter, experiments will be performed on the use of binary swelling solvents in molecular accessibility in coal conversion. David Tucker will be presenting an invited paper in the Symposium on Coal Conversion at the 45th ACS Southeast Regional meeting held in Johnson City, Tennessee and a second paper on The Use of Binary Swelling Solvent Systems in Coal Conversion.

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