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Molecular Accessibility in Oxidized and Dried Coals

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INTRODUCTION

The objective of this research project is to determine the molecular and structural changes that occur in swelled coal as a result of oxidation and moisture loss both in the presence and absence of light using our newly developed EPR spin probe method. The proposed study will make it possible to deduce the molecular accessibility distribution in swelled, oxidized APCS coal for each rank as a function of (1) size (up to 6 nm) and shape, (2) the relative acidic/basic reactive site distributions, and (3) the role of hydrogen bonding as a function of swelling solvents. The advantage of the EPR method is that it permits molecules of selected shape, size and chemical reactivity to be used as probes of molecular accessible regions of swelled coal. From such data an optimum catalyst can be designed to convert oxidized coal into a more convenient form and methods can be devised to lessen the detrimental weathering processes.

PREVIOUS WORK

Long-Term Weathering of APCS coal

A detailed study of long term weathering of 8 APCS coals using spin probe VII in toluene has been carried out. Preliminary results were given at the Symposium on Coal Conversion at the 45th ACS Southeast Regional meeting held in Johnson City Tennessee, October 17-20, 1993.¹

The intercalation of potential catalysts in APCS coal Illinois #6 during the swelling process in binary solvent mixtures² was studied using spin probes with various functionalities as model guest compounds.

An invited paper on the current status of spectroscopic techniques used to study the porous structure of coal with emphasis placed on the recent application of the EPR spin probe method to the study of Argonne Premium Coal Samples (APCS) was given by the principal investigator at the National ACS Meeting, Division of

Fuel Chemistry, Symposium³ on *Recent Advances in Coal Chemistry* in San Diego, CA March 13-17, 1994.

Results of long term weathering for periods up to six months of exposure to air have been analyzed for spin probes VI (3-carboxy-2,2,5,5-tetramethylpiperidine-1-oxyl) and VIII (TEMPO).³

It was determined³ that the medium ranked coals (Illinois #6 at 80.7% carbon and Blind Canyon at 81.3% carbon) are effected to a greater extent than the low or high ranked coals. Careful comparison of these results to the data obtained for vacuum dried coals oxidized in a pure oxygen environment has led to conclusions that the oxidative process for coals proceeds very similarly to autoxidation observed in polymers. The oxidative degradation of polymers proceeds by a method called hydroperoxide autoxidation.

Binary Swelling Results

Binary swelling data has been collected for all Argonne Premium Coal Samples (APCS). It appears from preliminary analysis that as the rank of the coal increases, and the presence of interconnected weak hydrogen bonds decreases, that the strong oscillatory behavior observed at low rank⁴ with increasing pyridine concentration, decreases markedly. For instance, the amount of included substituted amine nitroxide spin probe (a direct measure of the percent of hydrogen bonding) decreases substantially for swelled Upper Freeport compared to swelled Beulah Zap coal. An invited paper⁵ was given at the 26th Southeast Regional American Chemical Society meeting held in Birmingham, AL, October 16-17, 1994. The results to date⁵ for Upper Freeport and Lewiston-Stockton coals were discussed in light of the previous study of Wyodak-Anderson and Beulah-Zap coal.

It appears that the observed binary swelling data for the APCS coals studied to date can be explained in terms of four different processes: one, disruption of weak

hydrogen bonds which protect or isolate the interconnected micropore system; two, disruption of weak hydrogen bonds which protect individual micropores; three, the competition of pyridine for the active sites capable of establishing hydrogen bonds or the "poisoning" of active sites; four, disruption of stronger hydrogen bonds within the macromolecular structure which cause an opening of the structure. The contributions of each of these factors to the spin probe retention with increasing concentrations of pyridine vary up to 5% pyridine. At concentrations above 5% pyridine, the first factor becomes less significant, and variations in the others require greater changes in pyridine concentration.

O-alkylation

The presence of the internal hydrogen bonding, in particular its role in the bedding planes, plays an important role in determining the swelling characteristics in various ranked coal. To further examine the swelling behavior using the EPR spin probe technique, known O-alkylation procedures have been used to remove internal hydrogen bonding in APCS coal samples by derivatizing the hydroxyls.⁶ Removing the internal hydrogen bonding prevents the polar spin probe retention. On the other hand, an increase in coal swelling by nonpolar solvents such as toluene has been observed. By swelling O-alkylated APCS coals swelled in nonpolar

as well as polar solvents using spin probes VII and VIII

yield the spin probe retention as a function of rank when internal hydrogen bonding due to hydroxyls is removed.

Preliminary results have been obtained for the O-alkylated APCS coals Beulah-Zap, Illinois #6, Upper Freeport, Blind Canyon, and Pittsburgh #8. The O-alkylation procedure is very tedious and progress has been slow.

SUMMARY OF CURRENT ACTIVITIES

Special care was taken this quarter to measure the uptake of nitroxide spin probes in alkylated coal of the Lewiston-Stockton (LS) and Wyodak-Anderson (WA) seams. A key concern is the reproducibility of the relative spin probe concentration. It has been found that O-alkylation removes the polar hydrogen bonding – so the non-polar toluene now becomes a better solvent. This was observed by the fact that an increase in spin probe concentration by a factor of 4 for LS and a factor of 2 for WA occurred when toluene was used as the solvent. However it is very important to note that the 100% swing in uptake of spin probe as a function of a trace amount of pyridine (<5%) in toluene observed for unalkylated coal is absent for alkylated WA and LS coals. The variation in nitroxide spin concentration with pyridine concentration has in alkylated coal has been reduced to a 5-10% effect. These results support the previous mechanism where trace amounts of pyridine break up the local hydrogen bonded structure and either provide for an increase in accessibility in a local area where the spin probe may become attached or increase the size of the pore so that the spin probe gets washed out.

Two short papers are being written which will appear in the *Preprint Papers of American Chemical Society, Division of Fuel Chemistry*. These papers entitled "Influence of Binary Swelling Solvents: Mechanism of Action" and "Swelling Behavior of O-alkylated APCS Coals as Examined by the EPR Spin Probe Method" will be given at the fall meeting of the ACS as part of two symposia in the Fuel Chemistry Division.

STUDIES PLANNED FOR NEXT QUARTER

Since reproducibility is always a concern in the study of such heterogeneous material as the APCS coals, alkylated samples of Blind Canyon and Illinois #6 coal

will be reexamined. Samples of alkylated Pocahontas #3 are now being prepared and the results will be given next quarter.

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