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.\(^1\) The intercalation of potential catalysts in APCS coal Illinois #6 during the swelling process in binary solvent mixtures\(^2\) 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 has been presented.\(^3\) Results of long term weathering for periods up to six months of exposure to air have been analyzed for spin probes VI (3-carboxyl-2,2,5,5-tetramethylpiperidine-1-oxyl) and VIII (TEMPO).\(^3\)

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 decrease that the strong oscillatory behavior observed at low rank\textsuperscript{4} with increasing pyridine concentration, decreases markedly. The results to date for Upper Freeport and Lewiston-Stockton coals were discussed\textsuperscript{5} 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.

\textbf{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.\textsuperscript{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 \[ \text{H}_2\text{N}-\text{N-O} \] and VIII \[ \text{N-O} \]
yield the spin probe retention as a function of rank when internal hydrogen bonding due to hydroxyls is removed.

Papers have been published on the Influence of Binary Swelling Solvents and on the Swelling Behavior of O-Alkylated APCS Coal. It was found that upon O-alkylation, the hydrogen bonding is removed and the microporous structure increases in size. The strong oscillatory variation in spin concentration as a function of percent pyridine in a toluene swelling solvent was eliminated. A paper has been accepted for presentation in the coal Liquefaction/Coprocessing Symposium for the National ACS meeting to be held in Orlando, FL, Aug. 25-29 entitled "Changes in Molecular Accessibility in APCS Coal Oxidized in the Presence of Sunlight." This study was carried out for Pocahontas #3, Lewiston-Stockton and Wyodak-Anderson coal in which the oxygen content varies from 2% to 17%.

SUMMARY OF CURRENT ACTIVITIES

A study has been carried out to examine the weight loss of Wyodak-Anderson Lewiston-Stockton, Pocahontas #3 and Illinois #6 left in air as a function of time in the presence and absence of light. It has been found that the presence of sunlight accelerates the weight loss and in general a greater percent weight loss occurs as the oxygen content increases (See Figure 1).

The effect of sunlight on the weathering of APCS coal is currently being carried out for Beulah-Zap (~20% oxygen content), Illinois #6 (~14% oxygen content) and upper Freeport coal (~8% oxygen content). Plots of spin probe concentration for coal swelled in toluene versus time of exposure to air in the dark, versus time of exposure to air in the presence of sunlight and versus time of exposure to air in the presence of sunlight and then alkylated are being recorded. From such data, in addition to that already recorded, the effect of oxygen present in the coal, exposure to air and to sunlight will be deduced. Some difficulty is being experienced in the
alkylation of Beulah-Zap and Illinois #6 coals. Possible solutions to the preparation problems are being tried.

STUDIES PLANNED FOR NEXT QUARTER

The effect of sunlight on the weathering of Beulah-Zap in the absence and presence of sunlight and after being alkylated will be completed.

REFERENCES

Lost Weight Dependents Upon The APCS Coal

The APCS Coals were in the dark air

The APCS Coals were in sunlight

(A) The APCS Coals were in the dark air

(B) The APCS Coals were in sunlight