DOE Report No. DOE/PC/93202-13

December, 1996
Quarterly Report
For
Grant No. DE-FG22-93PC93202
entitled

Molecular Accessibility in Oxidized and Dried Coals

Lowell D. Kispert, Principal Investigator
Department of Chemistry
The University of Alabama
Tuscaloosa, AL 35487-0336

US/DOE Patent clearance is not required prior to the publication of this document.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
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 EPR spin probe method. The proposed study will make it possible to deduce the molecular accessibility distribution in swelled, oxidized APCS coal as a function of sunlight 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 reported.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 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). As the rank of the coal increased, the presence of interconnected
weak hydrogen bonds decreased and the strong oscillatory up-take of spin probes as a function of percent pyridine in toluene swelling-solvent observed at low rank with increasing pyridine concentration, decreases markedly. The results to date for Upper Freeport and Lewiston-Stockton coals were presented in light of the previous study of Wyodak-Anderson and Beulah-Zap coal.

Analysis of the 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

To further examine the swelling behavior in the presence or absence of internal hydrogen bonding 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. 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 in nonpolar as well as polar solvents using spin probes VII
When internal hydrogen bonding due to hydroxyls is removed, the spin probe retention as a function of rank yields the spin probe retention as a function of rank.

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 was presented in the coal Liquefaction/Coprocessing Symposium of the National ACS meeting 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 varied from 2% to 17%. A paper subsequently published (reprint attached) on the topic examined the reason that sunlight played an important role in the weathering process. One possible reason is the formation of singlet oxygen by energy transfer from the excited singlet states of the naturally occurring naphthalene and phenoxy anion radical in the coal to the singlet excited state of oxygen.

Last quarter (September report) the effect of sunlight on the weathering of APCS coal was reported for Beulah-Zap (~20% oxygen content), Illinois #6 (~14% oxygen content) and Upper Freeport coal (~8% oxygen content). A decrease in spin probe uptake by a factor of two over that found for exposure to air in the absence of light was observed to occur for Beulah-Zap. No dependence on sunlight was detected for Illinois #6 and an approximate 50% increase in spin probe uptake occurred for Upper Freeport upon exposure to sunlight over a 10 hour period. Two mechanisms, cross-linking versus the increase in functional groups were evoked to explain these results. Unfortunately, the September, 1996 report contains an error;
Figures 1 and 2 need to be interchanged. It appears that the trend as a function of oxygen content in the coal follows the same dependence as found earlier for Pocahontas #3, Lewiston-Stockton and Wyodak-Anderson. So far it has been determined that the microporosity depends on the structure of the coal; coals with similar percent oxygen content do not show the same percent increase in microporosity. In oxygen rich coal, evidence exists for crosslinking as a function of exposure to air and sunlight.

**SUMMARY OF CURRENT ACTIVITIES**

This quarter, the uptake of spin probe VII was measured for Upper Freeport (C = 86% and O = 8%) after the sample had been exposed to air and sunlight and then alkylated. In Figure 1 is plotted the uptake of spin probe VII as a function of time in the absence of light. A decrease of 25% in uptake of spin probe VII occurred over an eight hour period. In Figure 2 is the uptake in the presence of light and air as a function of time. A 30% increase in the uptake of VII occurred over an eight hour period as a result of more functional groups being present due to oxidation by air and sunlight.

Upon alkylation (Figure 3) a more open porous structure is present. A doubling (1.7 to $3.5 \times 10^{18}$ spin per gram) in the uptake of VII occurred in the absence of sunlight followed by an 8% increase in the uptake of VII over an eight hour exposure to sunlight. This is in contrast to O-alkylated Upper Freeport in the absence of air oxidation and sunlight-reported earlier (Figure 4) where a 50% increase in uptake of VII occurred upon swelling in pure toluene.

The data in Figure 1, demonstrates that with time, the micropore structure in Upper Freeport coal increases in size, causing the loss of spin probe VII upon washing with cyclohexane. This is consistent with the properties of a poor swelling solvent. The increase in uptake of spin probe VII upon exposure of the Upper
Freeport coal to sunlight confirms the importance of singlet oxygen in coal oxidation as suggested in an earlier paper.\textsuperscript{10}

Upon alkylation, it was previously deduced that cross-linking by the combination of hydroperoxide radicals with radicals existing in the coal occurred for oxygen rich Wyodak-Anderson and also presumably - Beulah-Zap. As the time of exposure to sunlight increased a decrease in molecular accessibility (decrease in spin probe VII uptake) occurred due to an increase in cross-linking character. However for high rank coal Upper Freeport, this effect was not present to any significant degree and the increase presence of functional groups as deduced by alkylation and subsequent hydrogen bonding caused an increase in the uptake of polar spin Probe VII. These two mechanism essentially counter-balanced each other for Lewiston-Stockton or in the present case of Illinois #6. Further study of this effect will require alkylation of the other coal samples after exposure to sunlight.

STUDIES PLANNED FOR NEXT QUARTER

The uptake of spin probe VII will be measured for Beulah-Zap after the sample has been exposed to air and sunlight and then alkylated. This will give some measure of the hydrogen bonding that contributes to the molecular accessibility in high rank coal.

REFERENCES


Figure 1. Uptake of spin probe VII in Upper Freeport coal swelled in toluene after exposure to air in the dark as a function of time. The dashed line is the straight-line average and the solid line is merely a connection of the experimental points.

Figure 2. Uptake of spin probe VII in Upper Freeport swelled in toluene after exposure to air in the presence of sunlight as a function of time. The dashed line is the straight-line average and the solid line is merely a connection of experimental points.
Figure 3. Uptake of spin probe VII in Upper Freeport coal swelled in toluene after exposure to air and sunlight as a function of time followed by alkylation. The dashed line is the straight-line average and the solid line is merely a connection of the experimental points.

Figure 4. Uptake of spin probe VII in O-alkylated Upper Freeport coal in the absence of air and sunlight swelled in toluene.