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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.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-carboxy-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 rank⁴ with increasing pyridine concentration, decreases markedly. The results to date for Upper Freeport and Lewiston-Stockton coals were discussed⁵ 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.

It was observed that upon O-alkylation an increase occurred in spin probe concentration by a factor of 2.5 for Blind Canyon, an increase of 4 for Illinois #6 and 1.5 for Pittsburgh #8. If Illinois #6 coal was exposed to the sunlight for 1.5 hours before it was alkylated -- the retained spin probe concentration doubled over that kept in the dark -- implying that more sites of hydrogen bonding were removed, giving rise to a larger microporous structure. The strong variation in spin probe concentration as a function of percent pyridine observed when fresh coal samples were exposed to a binary swelling solvent of pyridine in toluene, was eliminated upon O-alkylation.

Papers have been published on the Influence of Binary Swelling Solvents⁷ and on the Swelling Behavior of O-Alkylated APCS Coal.⁸ 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.

SUMMARY OF CURRENT ACTIVITIES

This quarter a paper was given at the Joint SE/SW Regional ACS meeting held in Memphis, Tennessee, November 29 - December 1, 1995 on the swelling behavior for the O-alkylation of all eight APCS coals: Upper Freeport, Wyodak-Anderson, Illinois #6, Pittsburgh #8, Pocahontas #3, Utah Blind Canyon, Lewiston-Stockton and Beulah-Zap. It was verified that upon O-alkylation, the hydrogen bonding was removed and the microporous structure had increased in size.

We have continued to examine the effect of exposure of light before alkylation versus after O-alkylation of the coal structure. The variation in uptake of spin probe VII (amine group) is depicted in figure 1 for Wyodak-Anderson. Before O-alkylation, a significant decrease occurred in the uptake of VII with increasing

exposure to ambient light. This suggests that partial break-up of the hydrogen bond network occurs, making it possible to wash out more of the spin probes. This effect was eliminated if the coal was O-alkylated after exposure to sunlight (Figure 2). The removal of the source of hydrogen bonding is responsible for the lack of spin probe up-take variation with time of exposure to light. Further experiments have shown that the data in Figures 1 and 2 is reproducible with a deviation of less than $\pm 10\%$. It has also been observed that if Wyodak-Anderson coal is exposed to sunlight before swelling, the oscillatory up-take of spin probe VII as a function of percent pyridine is essentially removed.

STUDIES PLANNED FOR NEXT QUARTER

A paper will be presented at the National ACS meeting to be held in Orlando, Florida, August 25 - 29, 1996, on the influence of sunlight on the hydrogen bonding and oxidation properties of APCS Coals, Wyodak-Anderson, Lewiston-Stockton and Pocahontas Coal. Abstracts are due at the end of this next quarter. These three coals were selected because the oxygen content varies from 18% to 10% to 2%. Thus a wide variation in hydrogen bonding sites occur in these three coals. One possible mechanism is the formation of singlet oxygen as a result of energy transfer from the excited state of the radicals in undoped coal to the excited singlet state of oxygen. Thus one plausible cause for a change in oxidized products formed in coal upon exposure to sunlight is the formation and reaction of singlet oxygen. Further studies are in progress to examine this possible mechanism in greater detail.

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Figure 1: Time of exposure to sunlight versus retention of spin probes for Wyodak-Anderson Coal.

Figure 2: Time of exposure to sunlight versus retention of spin probes in Lewis-Stockton Coal after Alkylation. The coal samples were exposed to light and then alkylated.