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Molecular Accessibility in Solvent Swelled Coal

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PREVIOUS WORK COMPLETED:

An EPR technique developed in this lab¹⁻³ is being 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 added to the resulting solution, stirred over night at elevated temperature, filtered, washed with a nonswelling solvent to eliminate any spin probes that are not trapped in the pores and the spin concentration measured. Comparing these spin probe measurements to DRIFT data have shown⁴ that the relative number distribution of acidic functionalities can be accurately predicted by the spin probe method. The spin probe method has also been used to predict⁴⁻⁵ the increase in elongated voids in Pittsburgh No. 8 (APCS No. 4) upon swelling with pyridine in agreement with independent SANS data. NMR relaxation data show³ 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 temperature¹⁻³ and ENDOR measurements⁶ 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 and size to be used as probes of accessible regions of the coal, thus providing information on the importance of molecular shape.

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 the pore size distribution as a function of temperature when polar basic swelling solvents are used. APCS coals contain spherical pores when swelled at low temperature and with a mild swelling solvent. Upon swelling with hydrogen bonding solvents such as nitrobenzene or pyridine, pores become

elongated and cylindrical. The degree of elongation is dependent on both the polarity of the swelling solvent and the swelling temperature.

The talk we presented⁹ at the New York National ACS Fuel Division August '91 Symposium on novel analytical methods in the study of coal, based on the Ph.D. dissertation work of Ross Spears, pointed out the importance of solvent polarity in breaking up the hydrogen bonding between the bedding planes of the coal. It was shown that highly polar solvents such as pyridine can tie up the acid/base sites and prevent attack by polar molecules. Magnetic resonance imaging studies by Botto et al. at Argonne National Lab and Clarkson at the University of Illinois following our paper, showed MR data where the solvent was observed to occur in the bedding planes of the coal; confirming our results. The change in pore shape from spherical to cylindrical was found to be due to the anisotropy in hydrogen bond densities.¹⁰

This quarter a paper¹¹ was accepted in the Journal, *Fuel* on the micropore wall chemistry during swelling. It was found that for coals swelled in polar solvents, the decrease in spin concentration was associated with the decrease in hydrogen bond-type cross-link concentration with rank, and the increase in covalent cross-links. The decrease in hydrogen bond cross-link density in APCS coals was in turn associated with the decrease in oxygen functionality concentration, especially hydroxyl content, with rank. Spin probes with polar R groups showed selective retention over nonpolar spin probes of same size. Spin probe retention was dependent on the polarity of the R group, which proceeded in the order $-H \ll -OH < -CO_2H < NH_2$. Spin probe retention for moderately polar spin probes increased with swelling temperature for coals swelled in toluene. This increase was ascribed to hydrogen bond disruption by the spin probes. The most polar spin probe ($R = -NH_2$) showed no temperature effects up to 333 K, apparently because its R group

was strong enough to undergo significant hydrogen bond disruption at low temperature.

Swelling solvent polarity resulted in competition with polar spin probes for hydrogen bonding sites. Increasing the swelling temperature resulted in enhancement of solvent competition for hydrogen bonding sites. The effect of temperature was significantly greater as solvent polarity increased. It was shown that "acidity" and "basicity" were incorrect terms in considering coal micropore wall chemistry. The terms "hydrogen bond donor" and "hydrogen bond acceptor" were used instead. Polar spin probes interacted with coal primarily as hydrogen bond acceptors. Acidic spin probes showed some indication of acting as hydrogen bond donors, but the primary mechanism of interaction was as an acceptor.

Eight Argonne Premium Coal Samples (APCS) were weathered in air and the structural and chemical changes that occurred upon swelling with toluene and pyridine were examined by our EPR spin probe method. Under mild oxidation conditions and swelling with toluene large structural changes were observed for lignite (Beulah-Zap) which suggested the collapse of the coal structure. This did not occur for higher rank coal. Upon oxidation and swelling with toluene and pyridine an increase occurred in the amino substituted spin probe concentration for coals with the carbon percent above 80%. A maximum was found for the creation of 5 Å diameter pores upon swelling with pyridine at 85% C. These results were reported 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.

SUMMARY OF CURRENT ACTIVITIES

This quarter, a paper was published¹² on our study of the changes in the molecular accessibility in solvent swelled APCS coals that had been oxidized over a period of 6 months in ambient air with the humidity of less than 50%. An extensive study by David Tucker, a graduate student working for his Ph.D. degree, is nearing completion on the effect of oxidation of all 8 APCS coals over a period of 6 months in zero percent humidity. A more interesting study appears to be the oxidation process that occurs when the APCS coals are dehydrated in vacuum and then allowed to oxidized in ambient air with the relative humidity >60%. While fresh APCS coal oxidized in ambient air lose weight (25% for the lignite Beulah Zap and <1% for pocahontas); the vacuumed dried coal gained weight. David Tucker is currently analyzing his data on oxidation processes in the absence of water and in the presence of high humidity and will soon be able to present the full picture of the oxidation processes as a function of humidity and temperature.

W. Sady, a very productive visiting scientist has returned to Poland so he could return to university teaching. Preliminary drafts of several of his papers are now in preparation. In addition to his oxidation work, studies were carried out to examine the effect of dehydration at room temperature as well as 100°C. No differences were observed between coal dehydrated in vacuo at room temperature and at 100°C. Significant differences occur in the amount of spin probe concentration imbibed in the coal as a function of swelling temperature and spin-probe. At 60°C the spin-probe concentration was greater for the polar probes ($R = OH$, $COOH$ and NH_2) than for room temperature swelling presumably due to hydrogen bond breaking for coal swelled in toluene and nitrobenzene. The effect was diminished for coals swelled in pyridine. A maximum spin probe concentration occurred for 80% C. Dehydration of the lignite coals (74 and 76% C) indicated collapse of the coal structure and the

decrease in swelling by toluene or nitrobenzene solvent as evident by the significant decrease in spin-probe concentration. On the other hand a large increase in spin-probe concentration occurred with pyridine swelling.

STUDIES PLANNED FOR NEXT QUARTER

The primary goal will be to complete the analysis of the approximately 1000 EPR spectra so a preliminary report can be given on the effect of humidity on long term coal oxidation. Some evidence exists that oxidation for less than 1 day and as short as 2 minutes may produce measurable changes in the swelling characteristics of coal. If time permits, the effect of short ambient air oxidation will be studied.

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