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Molecular Accessibility in Solvent Swelled Coal

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PREVIOUS WORK COMPLETED:

An EPR technique developed in this lab[1-3] 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 shown[4] 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 predict[4-5] 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 show[3] 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 temperature[1-3] and ENDOR measurements[6] 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 in this area, it is the objective of our current study to determine molecular accessibility in Argonne Premium Coal Samples (APCS) upon swelling in polar, basic solvents before and after moisture loss. 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 are formed that are elongated and cylindrical due to the break-up of the hydrogen bonding between the bedding planes. The degree of elongation is dependent on both the polarity of the swelling solvent and the swelling temperature.

The talk we presented[9] at the New York National ACS Fuel Division August 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 catalysts. Magnetic resonance imaging studies by Botto 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. It was also shown that as the hydrogen bonding ability of the probe increases, the degree of probe retention increases, however; probe retention decreases with rank.

SUMMARY OF CURRENT ACTIVITIES

The EPR-spin probe method was used to study the swelling of covalently cross-linked 2%, 4%, 6% 8% and 12% polystyrene-divinyl benzene copoloymers, used as models of APCS coal structural elements. The results were compared with swelling studies on APCS coals and confirmed results showing that coal was polymeric, that it had covalent cross-links increasing with rank, that it was structurally anisotropic, and that its swelling was anisotropic.

A paper has been submitted to and reviewed for the journal *Fuel* on the low temperature swelling of Argonne Premium Coal Samples using solvents of varying polarity. The variation in the shape of the pore was followed as a function of temperature and swelling solvent polarity. This change in pore structure was attributed to break-up of the hydrogen bonding network in coal by polar solvents. The modification in pore shape from spherical to cylindrical was attributed to anisotropy in hydrogen bond densities.

Wojciech Sady has determined the structural changes in coal pores that occur when APCS coal is dehydrated prior to swelling with polar solvents. These changes are different from those that occur in the absence of prior dehydration. Most impressive is the huge change that occurs in lignite coal (Beulah-Zap). It appears that this coal has collapsed upon dehydration preventing any spin probe from being trapped in the dehydrated lignite upon swelling. Various sized probes have been studied. He has also completed a study on the variation in the hydrogen bonding character of the pore wall as the coals are swelled with various polar solvents. A statistical analysis of the data has been completed to determine important trends in his data. A paper is now in preparation to be submitted to Fuel.

During this next period we will be examining the changes in the swellability of the APCS coals upon oxidation and plan on submitting two papers to Fuel.

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