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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 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 pores 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

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swelling temperature. Results just reported⁹ in the August Fuel Division Symposium on the use of novel analytical methods in the study of coal properties at the national ACS meeting, showed that as the hydrogen bonding ability of the spin probe increases, the degree of probe retention increases, however, probe retention decreases with rank. Pyridine interacts specifically with polar functional group on the micropore wall and prevents binding with polar guest molecules.

SUMMARY OF CURRENT ACTIVITIES

A paper has just been submitted to 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. A copy of this paper has been attached to this report.

Wojciech Sady has determine the structural changes in the 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. 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 is currently underway to determine important trends in his data.

The talk we presented at the Fuel Division August Symposium in New York, pointed out the importance of solvent polarity in breaking up the hydrogen bonding between the bedding planes of the coal and the interference that highly polar solvents can cause in tying up the acid/base sites and preventing attack at these sites 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.

Recently, Ross Spears has completed a study of 2%, 4%, 6%, 8% and 12% cross-linked Biobeads using the EPR spin-probe technique that showed coal can not be considered just a highly crossed linked polymer and possess swelling properties predicted by standard polymer theory.

During this next reporting period we will include a full report on the results of Mr. Sady dehydration study and the swelling of biobeads.

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