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Molecular Accessibility in Solvent Swelled Coal

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DISCLAIMER

BACKGROUND:

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.

Summary of Current Activities

Dr. Lidia Piekara-Sady from the Institute of Molecular Physics in Poznan, Poland has begun carrying out the ENDOR study of the spin probe doped Argonne

Premium Coal Samples (APCS #3, #4, #5, #6 and #8) swelled with the solvents toluene, nitrobenzene and pyridine. Although ENDOR spectra are being obtained, methods are being developed to improve the ENDOR signal to noise so a more complete study can be obtained. Mr. Ross Spears, a graduate student working towards his Ph.D. degree in chemistry with speciality in coal chemistry has been carrying out a study of the changes in the size and member distribution of the accessible regions of the APCS coals #3, 4, 5, 6, and 8 as a function of rank upon swelling with solvents, toluene, nitrobenzene and pyridine using spin probes V, X, XII and XIII. So far he has found that as the basicity of the solvent increases (toluene to that of pyridine), the number and length of the cylindrical pores increased with decreasing rank. The number of cylindrical pores also increased with oxygen content (with decreasing rank) suggesting a destruction of the hydrogen-bond network upon swelling with pyridine. A paper based on this work has been accepted as a chapter to be published in an ACS Book entitled "Magnetic Resonance of Solid Carbonaceous Fuels." Mr. Spears actually started his Ph.D. dissertation research on the changes in coal porosity with swelling solvent approximately 9 months before the grant was awarded. Thus more than the usual progress can be reported for the first quarterly report.

These same studies are being extended to APCS #1, 2 and #7 coal samples. The pore size, shape and number-distribution will also be studied as function of the temperature at which the overnight swelling treatment is carried out.

No problems have developed so far other than the increasing difficulty in locating the spin probes of the size and shape needed to determine the changes in pore structure. The previous three year DOE - coal grant provided us with the support needed to set-up a functioning lab and support for trained personal to carry

out coal studies. Thus it should be possible to continue making progress during the next quarter.

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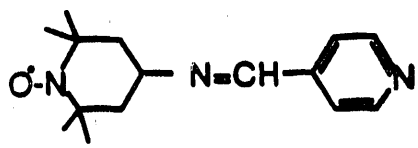
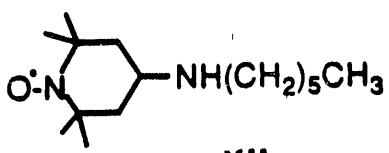


X



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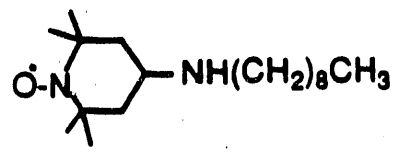

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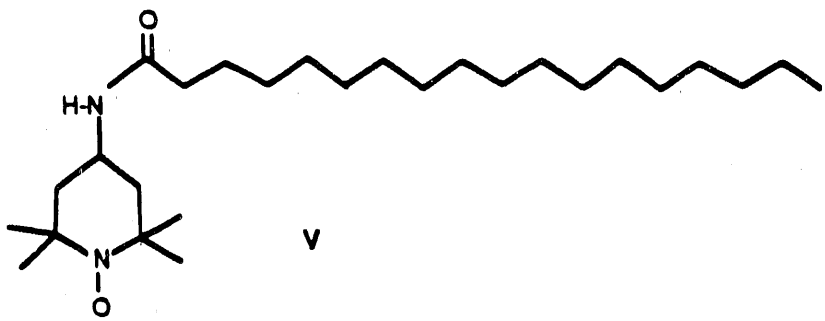

V

Spin Probes V, X, XII and XIII

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