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CATALYST ACCESSIBILITY IN HIGH VOLTATILE BITUMINOUS COAL

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OVERVIEW OF ACCOMPLISHMENTS:

As reported (DOE/PC/90502-1 to 12), an EPR technique has been developed in this lab to determine the pore size and number distribution in high volatile bituminous coal using nitroxide spin probes I-XIII of different sizes, shapes and reactivity. We have studied pore size and shape distribution in Mary Lee, Black Creek and Pratt coal from Alabama,[1,2] the Penn State Coals, PSOC #271, 137 and 669[2] as well as PSOC-1354 and PSOC-311[3] and Argonne Premium Coal Samples (APCS) #3, #4, #5, #6 and #8.[4-7] These coals were studied because independent SANS, DRIFT and NMR relaxation studies related to pore size and shape distribution have been recently reported which substantiated our results. SANS (small angle neutral scattering) studies, have been carried out for APCS #4 from which the changes in the pore structure upon swelling with different solvents were deduced. NMR spin-lattice relaxation measurements resulted in a pore size distribution before exposing the coal samples to various solvents. The relative number distribution of acidic functionalities deduced by the EPR spin-probe method for APCS #3, #4, #5, #6, and #8 was shown to be linearly related to the ratio of phenolic to alkyl OH groups determined by DRIFT measurements.[5] In addition, the predicted increase in elongated voids in APCS #4 upon swelling with pyridine was confirmed and studies as a function of rank correlate well with the distruction of the hydrogen bond network as a major reason for the change in pore shape. The accessibility of pore volume studied using spin probes with differing shapes shows a dependence on carbon content similar to that obtained from other measurements. ^{14}N and ^{1}H ENDOR spectra have been obtained for the first time from the nitroxide spin probe-doped Argonne Premium Coal Samples (APCS) #3, #4, #5, #6 and #8.[6] Proton matrix matrix ENDOR signals[6] at the free proton frequency, a broad ENDOR signal due to dipolar couplings between the radicals in undoped coal and the matrix protons, and proton ENDOR lines resulting from interaction of the surrounding matrix coal protons with the spin probe have been observed. This later result substantiates an earlier report of hydrogen bonding to the nitroxide spin probe.

An EPR spin probe method[7] was used to examine the changes in the size and number distribution of the accessible regions in five Argonne premium coal samples (APCS No. 3, No. 4, No. 5, No. 6, and No. 8) as a function of rank upon swelling with the solvents, cyclohexane, toluene, nitrobenzene, and pyridine. As the basicity of the solvent increased (toluene to that of pyridine), the number and length of the cylindrical pores increased with oxygen content (with decreasing rank) suggesting a destruction of the hydrogen-bond network upon swelling with pyridine.

A listing of the articles and presentations generated by this grant are given below. A copy of each article published or in press is attached for detailed examination. One remaining paper is now in final preparation to be submitted to Fuel. Mr. Ross Spears, a Ph.D. candidate is carrying out swelling studies as a function of pK_a. It is his goal to carry out a careful study of APCS #3, #4, #5, #6 and #8 to determine the change in pore shape and size distribution as a function of polar, basic swelling solvents that vary with pK_a such as tetramethyleneimine, pyridine, 2-fluoropyridine as well as a function of non-swelling solvent cyclohexane. These studies are giving us additional insight into the process of coal swelling and supplement the studies of Larsen and Hall.

SUMMARY:

The change in the relative pore size distribution in APCS No. 3, No. 4, No. 5, No. 6 and No. 8 as a function of rank and oxygen content upon swelling with different solvents can be followed by the use of the EPR spin-probe method. Linear fits were found between the increasing concentration of trapped cylindrical and spherical spin probes (for pyridine as the swelling solvent) and the increasing percent oxygen content of the coal. This dependence on oxygen content confirms the hypothesis that pyridine swells coal by breaking of hydrogen bonds. The acidic site distribution determined by EPR measurements is in complete agreement with that deduced from the DRIFT data. The EPR spin-probe method can also be used to

observe changes in the hydrogen bond structures of different coals and its success is due to the wide variety of functional groups and size of the spin probes that are possible. Proton ENDOR spectra can be observed for spin probe doped APCS No. 3, 4 and 6 from which the interaction between matrix coal protons and the nitroxide probe can be deduced.

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1. Wuu, S. K.; Kispert, L. D. *Fuel* **1981**, 64, 1681-1686.
2. Kispert, L. D.; Cooray, L. S.; Wuu, S. K. *Preprints, Fuel Chem. Div., Am. Chem. Soc.* **1987**, 32, 286-292.
3. Cooray, L. S.; Kispert, L. D.; Wuu, S. K. *Preprints, Fuel Chem. Div. Am. Chem. Soc.*, **1988**, 33, 32-37.
4. Goslar, J.; Cooray, L. S.; Kispert, L. D. *Fuel,* **(1989)**, 68, 1402.
5. Goslar, J.; Kispert, L. D., *"Energy and Fuel,"* **1989**, 3, 589-594.
6. Goslar, J.; Kispert, L. D., *Fuel*, in press 1990 (Galley copy attached).
7. Spears, R.; Goslar, J.; Kispert, L. D., "EPR Spin Probe Studies of Porosity in Solvent Swelled Coal," *ACS Adv. in Chem. Series: Magnetic Resonance of Solid Carbonaceous Fuel*, Edt. R. Botto and Y. Sanada, 1991.

Reprints + Preprints removed

(Copies of 1-7 have been attached)

ARTICLES AND PRESENTATIONS

1. L. D. Kispert, L. S. Corray, and S. K. Wuu, "An EPR Study of Nitroxide Spin Probe Doped Illinois No. 6 Coal from the Premium Coal Sample Program: Reactive Site Distribution," *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **32(4)**, 286 (1987). Presentation given Sept. 3-4, 1987, at ACS National Meeting, New Orleans.

2. L. S. Corray, L. D. Kispert and S. K. Wuu, "An EPR Study of Pore Accessibility in Argonne Premium Coal Samples," *Am. Chem. Soc. Div. Fuel Chem Preprints,* **33(3)**, 32 (1988). Presentation given Sept. 25-30, 1988, at ACS National Meeting, Los Angeles.

3. J. Goslar, L. S. Corray, and L. D. Kispert, "An EPR Study of Pore Accessibility in High-Volatile Bituminous Coal: Solvent Dependence," *Fuel*, **68**, 1402 (1989).

4. J. Goslar and L. D. Kispert "Accessibility, Reactive Site Distribution and Swelling Properties of Argonne Premium Coal Samples Studied by a Spin-Probe EPR Method," *Energy and Fuels*, **3**, 589 (1989).

5. J. Goslar and L. D. Kispert, "EPR and ENDOR Studies of Argonne Premium Coals Doped with Nitroxide Spin Probes" *Fuel*, in press 1990.

6. J. Goslar and L. D. Kispert "EPR Spin Probe Studies of Porosity in Solvent Swelled Coal," presented at the 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Dec. 17-22, 1989.

7. R. Spears, J. Goslar and L. D. Kispert, "EPR Spin Probe Studies of Porosity in Solvent Swelled Coal," *ACS Adv. in Chem. Series: Magnetic Resonance of Solid Carbonaceous Fuel*, Edt. R. Botto and Y. Sanda, 1991.

8. R. Spears and L. D. Kispert, Changes in the Pore Structure of Argonne Premium Coal Samples Under Mild Swelling Conditions: An EPR Spin Probe Study in preparation.

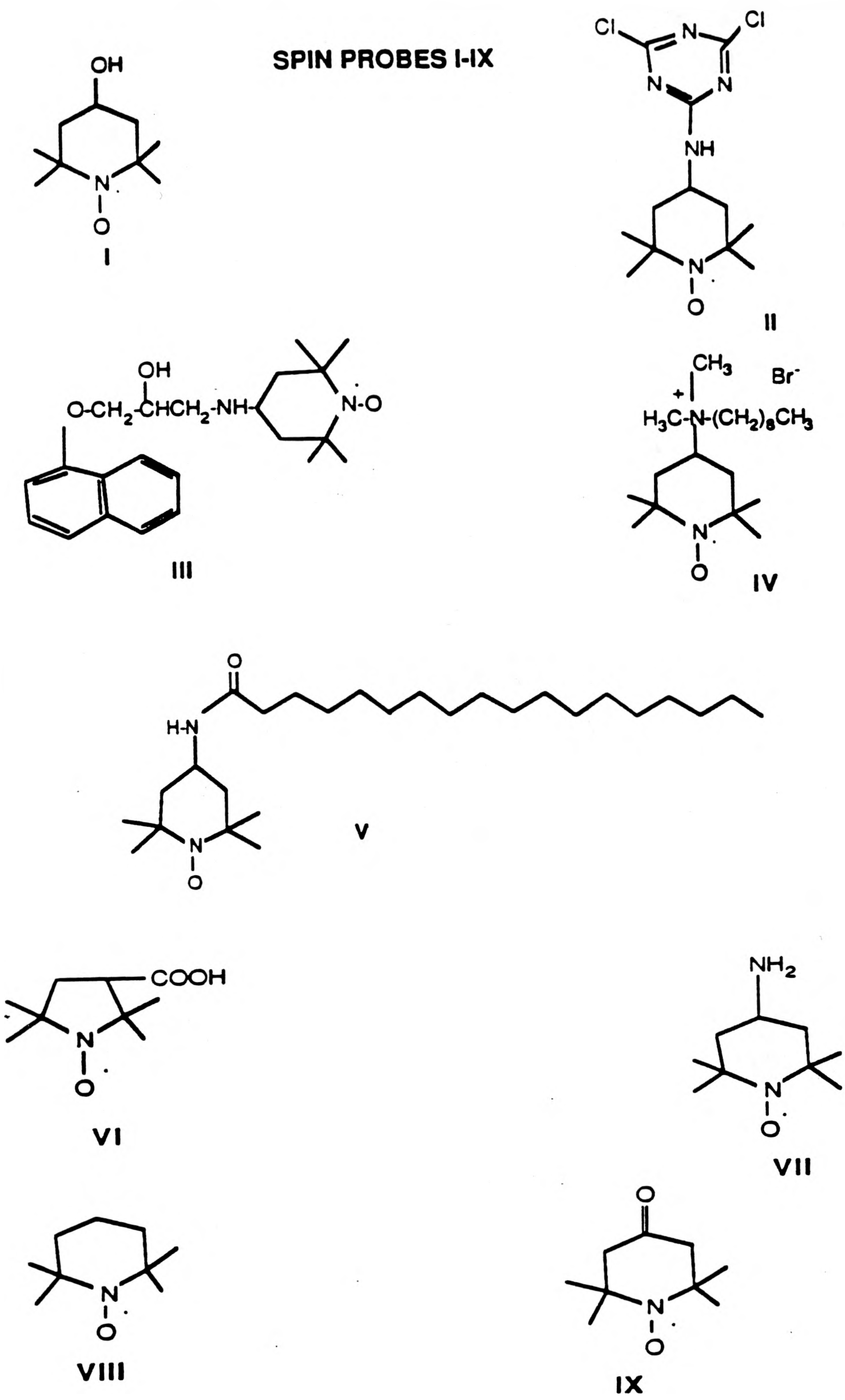
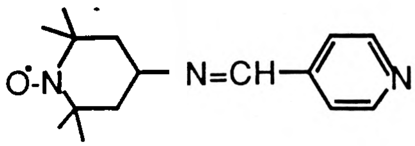


Figure 1.



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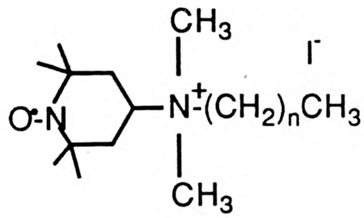

XI

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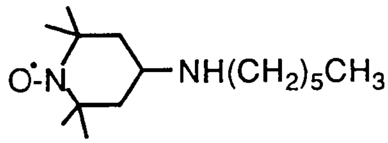
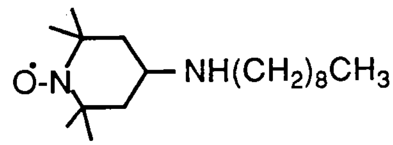


XII



XIII