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INVESTIGATION OF OXYGEN FUNCTIONAL GROUPS IN LOW RANK COAL

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INTRODUCTION

The distribution of the organic oxygen content of coals among the principal oxygen containing functional groups typically is determined by a combination of chemical and spectroscopic methods *(1,2)* and results in a classification scheme such as % carboxyl, % hydroxyl, % carbonyl, and % ether. A notable subdivision in this classification scheme is the differentiation of phenols in a coal on the basis of their *ortho*-substitution pattern *(3)*. Apart from this distinction, the further classification of oxygen into functional group subsets is virtually nonexistent. This paper presents initial experiments that indicate a fuller characterization of oxygen distribution in low rank coal is possible.

The experimental approach couples selective chemical perturbation and solid state NMR analysis of the material, specifically, the fluorination of Argonne Premium Coal #8, North Dakota lignite, and spectroscopic examination by high resolution solid state ^{19}F NMR *(4)*. The fluorination reagent is diethylaminosulfur trifluoride (DAST), $(Et)_2NSF_3$, which promotes a rich slate of oxygen functional group interconversions that introduce fluorine into the coal matrix *(5)*. The virtual absence of this element in coals make ^{19}F an attractive NMR nuclei for this application *(6)*. The present experiments use direct detection of the ^{19}F nucleus under conditions of proton (^1H) heteronuclear dipolar decoupling and magic angle spinning (MAS). The ca 300 ppm range of ^{19}F chemical shifts in common carbon-fluorine bonding configurations and high ^{19}F nuclear sensitivity permit the identification of unique and chemically dilute functional groups in the coal milieu. The unique detection of aromatic and aliphatic carboxylic acids and primary and secondary alcohols provide examples of the exquisite functional group detail that is revealed by this combination of techniques.

RESULTS AND DISCUSSION

DAST Chemistry. Diethylaminosulfur trifluoride, $(Et)_2NSF_3$, is an easily handled liquid cognate of SF_4. The chemistry of this reagent has been reviewed in depth.[5] DAST effects a wide range of oxygen replacement chemistry. It is useful for the conversion of primary, secondary and tertiary alcohols into alkyl monofluorides, aldehydes and ketones into geminal difluorides, and free carboxylic acids into acyl fluorides. The dehydration of alcohols is a competing reaction path that accompanies conversion of alcohols into fluorides.

MASTER

The byproducts of the reaction of DAST with coal are hydrogen fluoride and thionyl fluoride. The hydrolysis of unconsumed DAST will produce diethylamine

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hydrofluoride. Secondary reactions between endogenous mineral or organic matter in the coal and HF may occur. The ^{19}F MAS NMR spectra of the fluorinated lignite reveals a complex pattern of resonances that are derived from both chemisorbed amd physisorbed species. The separation of these contributions in the ^{19}F spectrum is discussed in the following paragraphs.

Deposition of Et_2NH*HF on North Dakota lignite by room temperature evaporation from $CHCl_3$ solution produces a material whose spectrum consists of two resonances with relative intensities, halfheight width, and, for one resonance, peak position, that are dependent on coal preparation. The ^{19}F spectrum derived from the product of treatment of wet North Dakota lignite (as received APC#8) consists of two resonances: a sharp resonance, -129.4 ppm, from diethylamine hydrofluoride, and a resonance at -144 ppm with $v_{1/2}$ = 1600 Hz. Drying the coal prior to deposition gives a spectrum containing the resonance of diethylamine hydrofluoride and a broad resonance, $v_{1/2}$ = 6000 Hz, at -127 ppm. The material prepared from dry, demineralized lignite gives a spectrum similar to that using dry lignite except that the chemical shift of the broad, $v_{1/2}$ = 5900 Hz, component is -147 ppm.

Vacuum drying these co-deposited mixtures at 100°C for 15 h gives products that are largely free of fluorine (> 98%) relative to the non-evacuated coals. Hence, not only the -129 ppm resonance of diethylamine hydrofluoride, but also the broad variable shift peak derive from *volatile* fluorine species. The broad resonance is assigned to adsorbed HF. It is likely that the water in the coal, as received, increases the mobility of HF on the coal surface and attenuates surface structure differences, producing a narrower resonance for HF in the wet lignite.

Long term acquisition on the evacuated sample yields a low signal-to-noise spectrum that has broad resonances at ca -120 +/- 10 and -140 +/- 10 ppm. Water washing this sample results in a slight decrease in the intensity of the resonance at ca. -120 ppm but otherwise has little effect on the spectrum. These resonances are attributed to chemisorbed species that result from the reaction of HF with functional groups in the organic matrix of the coal.

The Reaction of DAST with North Dakota Lignite. The reaction of DAST with demineralized lignite has been run under a variety of experimental conditions that alter time, temperature and solvent. The fluorinated materials yield spectra which differ in detail. Figure 1 presents a series of spectra obtained as a function of reaction temperature. As the reaction temperature is raised the extent of fluorine incorporation increases. At the lowest temperature, -40°C, the dominant feature in the spectrum is the acyl fluoride resonance (lower trace). **The resonance is a partially resolved doublet at +44 and +30 ppm which represents aliphatic and aromatic carboxylic acid fluorides, respectively.** The ^{19}F MAS NMR spectrum, by virtue of its nuclear and chemical shift sensitivity, make the distinction between these functional group subsets possible. The first upper and lower spinning sidebands are resolved in this spectrum as is the second lower sideband. The centerband/sideband intensity ratios are similar to model acyl fluorides and reflect the large ^{19}F chemical shift anisotropy of fluorine in this bonding configuration.

The -40°C spectrum also shows an incipient resonance band for primary alkyl fluorides, -220 ppm, and a prominent band for secondary alkyl fluorides, -182 ppm. A narrow resonance at -124 ppm, likely arising from residual amine hydrofluoride salt, is superimposed on a broad ill-defined resonance band. This sample has undergone little chemical perturbation, with the introduction of 0.18 wt % fluorine. Variable MAS experiments on this sample show that all of these resonances are centerbands.

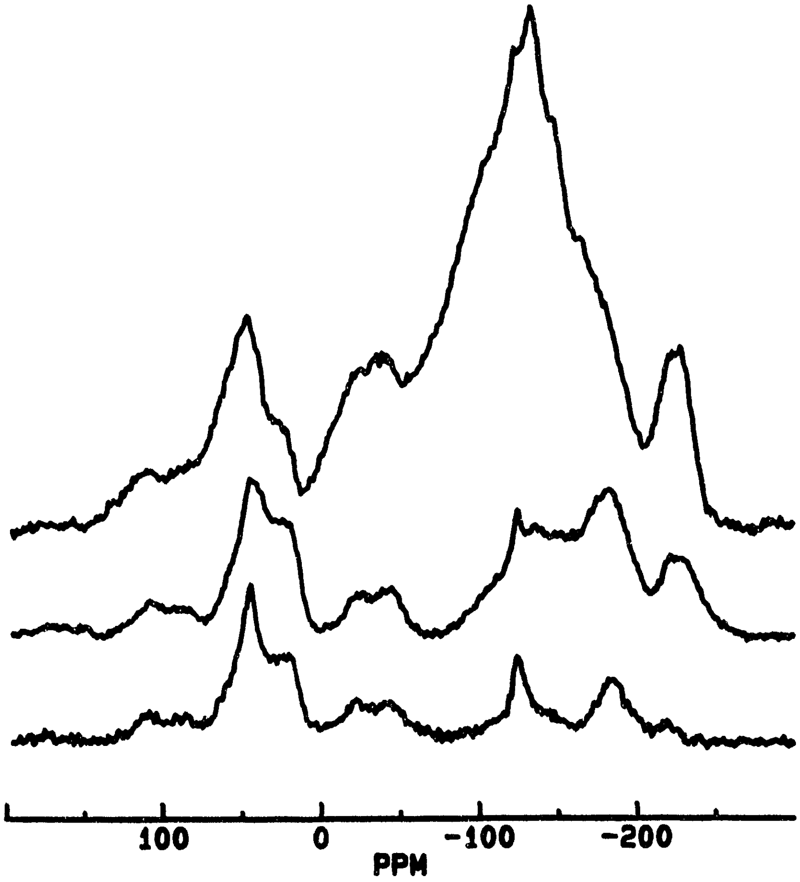

Fig. 1. ^{19}F MAS NMR spectra of DAST-fluorinated North Dakota lignite as a function of reaction temperature: upper trace, R.T.; middle, 0°C; lower, -40°C.

Running the reaction at 0°C increases the fluorine content of the coal (0.54 wt %) and produces the ^{19}F spectrum shown in Figure 1 (middle trace). The acyl fluoride resonance and its sidebands remain a prominent feature of the spectrum though the dramatic change in the spectrum is the large increase in alkyl fluoride resonances. **Partially resolved resonances occur for primary, secondary and tertiary fluorides,** at -220, -182, and -135 ppm, respectively. The change in relative intensity of the acyl fluoride/alkyl fluoride resonance bands, with respect to the low temperature spectrum, is dramatic and indicates that the chemical selectivity of DAST can be controlled by reaction temperature.

DAST fluorination at room temperature produces a coal derivative with an 0.83 wt. % fluorine content. The spectrum of this material, Fig.1, upper trace, shows a large area increase, relative to the 0°C spectrum, centered at -100 to -130 ppm. The high field region, ca -130 ppm, is the extreme low field resonance limit of tertiary fluorides and abuts the chemical shift range of difluoromethyl resonances -110 to -130 ppm. The low field resonance range, -90 to -120 ppm, is that of difluoromethylene moieties. There is substantial resonance overlap in the regions for the difluoro species. The large CSA of the -100 ppm resonance, apparent through its recognizable first and second order sidebands, indicates the difluoromethylene moiety is the major functional group responsible for this resonance. This broad resonance band and its sidebands decreases overall resolution in the acyl fluoride and alkyl fluoride regions of the spectrum.

The spectra in Figure 1 demonstrate that the ^{19}F MAS NMR permits a characterization of oxygen functional groups via reaction with DAST. The extremes in oxidation state, i.e., primary alcohols and carboxylic acids, are the easiest to characterize, as their fluoride analogs lie at the extremes of the ^{19}F chemical shift range of organic fluorides and show minimal overlap with other fluorine functional groups. The partial resolution of aliphatic and aromatic carboxylic acid resonances, +44 and +30 ppm, respectively, holds the promise that these functional group subsets can be used to further characterize coal structure and reactivity.

The detection of primary fluoride resonances, -220 ppm, allows the first inference from solid state NMR measurements, of the presence of primary alcohol functions in this coal. This conclusion assumes that the primary fluoride resonance arises through the simplest and expected pathway, fluoride replacement of primary alcohols.

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