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A SOLID-STATE NMR STUDY OF CONDENSATION/RETROGRADE REACTIONS DURING COAL LIQUEFACTION

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BACKGROUND

The objective of this work is to perform an NMR study of the aromaticity in coals, coal derived products and/or model compounds generated by pyrolysis and thermal solubilization of coal in the presence of a hydrogen donor solvent. Cross Polarization with Magic-Angle Spinning (CP/MAS) will be used to measure the carbon aromaticity, and Combined Rotation and Multiple Pulse Spectroscopy (CRAMPS) NMR techniques will be used to measure the hydrogen aromatricity. From these NMR measurements the aromatic hydrogen-to-carbon ratio will be obtained and used to study condensation/retrograde reactions during coal liquefaction.

The study consists of four tasks: 1) develop NMR methods to determine aromatic carbon by CP/MAS and aromatic hydrogen by CRAMPS for low hydrogen containing organic solids such as coals, and coal residues; 2) characterize the feasibility of applying the NMR methods for quantitative measurements in coals; 3) analyze selected samples of coals and coal-derived products to demonstrate applicability of the NMR methods to study coal liquefaction, and 4) report the results to the Department of Energy.

ACCOMPLISHMENTS

The development of the CP/MAS and CRAMPS methods for coals is being done at the Colorado State University in Fort Collins, Colorado. During the quarter, work concentrated on development of the CP/MAS ^{13}C

techniques for quantitative carbon aromaticity measurements in coals. Two avenues for quantitation were pursued: 1) use of a large volume sample spinner, and 2) use of Delrin as a "built in" intensity standard for ^{13}C spin counting.

Large Sample ^{13}C NMR Spectroscopy of Coal

One of the main problems with ^{13}C MAS studies of coals, especially those employing the ^{13}C CP/MAS approach, has been uncertainty regarding the quantitative significance of the measured ^{13}C intensities. For any ^{13}C NMR experiment on coal, one of the issues responsible for some of the uncertainties is the uncharacterized role that the substantial concentrations of unpaired electrons (typically 10^{17} - 10^{19} spins/g) may have on the ^{13}C NMR experiment (1). In principle, such paramagnetic centers could broaden or shift the resonances of nearby ^{13}C nuclei beyond the usual limits of detection. For single pulse (SP) ^{13}C MAS experiments, there is also the possibility that some of the ^{13}C nuclei reside in locations that are so remote from relaxation sources that their ^{13}C T_1 values (T_1^C) are sufficiently large so as to preclude detection under the usual conditions (pulse repetition rates) that are employed. For ^{13}C CP/MAS experiments on coal, there is the additional uncertainty that some ^{13}C spins in condensed aromatic rings are so remote from the nearest hydrogen atoms that they are not cross polarized in a typical ^{13}C CP/MAS experiment.

Studies have addressed the issue of these "invisible carbons" in the ^{13}C CP/MAS experiment on coal and have concluded that a substantial fraction of carbons in coal is not detected by the CP/MAS technique (1-3). It has generally been believed that SP/MAS techniques should, in principle, be capable of providing quantitatively more reliable ^{13}C intensities for coal than CP/MAS techniques, because the "CP-invisible" carbon issue is avoided in SP experiments. Although a few ^{13}C SP/MAS experiments on coals have been reported (4), this approach has been severely hampered by S/N limitations, because the CP sensitivity enhancement of $\gamma_H/\gamma C \simeq 4$ is not available in a SP experiment. Attempts to enhance S/N by using high-field spectrometers have been largely thwarted by the large chemical shift anisotropies typical of the sp^2 (aromatic) carbon resonances in coal and the associated spinning sideband difficulties at high field (5).

In order to address the S/N difficulty in ^{13}C MAS experiments on coal in general, and especially in the SP mode, a large-volume (2.5 cm^3) MAS system that is routinely capable of MAS speeds of more than 4.0 kHz has been developed (6). This volume is roughly 4-6 times larger than the volume of a typical MAS sample container. The anticipated increase in S/N has been realized with this system. Also, the 4 kHz MAS speed is sufficient to largely eliminate spinning sidebands (<5%) in ^{13}C MAS experiments on coal at magnetic field strengths up to about 2.5 T. During the quarter the use of this large-volume MAS system for the study of a bituminous coal by SP/MAS and CP/MAS ^{13}C NMR techniques was investigated. In particular the increased S/N allowed for some pertinent aspects of quantitation to be addressed.

Solid-state ^{13}C MAS spectra were obtained at 22.6 MHz on a Chemagnetics M-100/90S spectrometer, using the large-volume Delrin-Zirconia spinner. T_1^H values were measured through ^{13}C signals via cross polarization (7). T_1^C values were measured by inversion-recovery techniques, a) using a long delay time between repetitions and spin-lattice relaxation for generating the ^{13}C magnetization to be inverted and b) after generating ^{13}C magnetization by cross polarization. T^{CH} and T_{1p}^H values were determined from variable contact-time experiments.

The coal studied was an eastern bituminous coal from the Powhatan No. 5 mine. The elemental analysis of this coal (dry) was: C, 72.25%; H, 4.94%; N, 0.83%; Cl, 00.07%; S, 3.66%; O, 6.88% (difference); ash, 11.57%.

Single pulse, SP/MAS, and cross polarization, CP/MAS, spectra were obtained on Powhatan coal for different pulse delay times. Overall, the different spectra showed similar relative intensities and S/N values. The SP/MAS spectra yielded slightly higher carbon aromaticity values than those obtained by CP/MAS. However, a good SP/MAS spectrum required about 5 hours to obtain, whereas a CP/MAS spectrum was obtained in about 5 minutes.

In order to assess the quantitativeness of the SP-and CP/MAS NMR methods, the pertinent NMR relaxation times were measured (Table 1). The favorable S/N characteristics of the large volume MAS system provided an excellent opportunity to measure these parameters, especially for the SP experiments which require considerably longer times.

An important result of the relaxation time measurements is that a substantial fraction (~0.50) of the sp^2 (aromatic and carbonyl/carboxylate) carbons have spin-lattice relaxation times of about 34s. This means that pulse delays of greater than 100s should be used to minimize intensity distortions in the SP/MAS experiments.

The proton spin-lattice relaxation times, T_1^H, are 122 ms and 120 ms for the aromatic and aliphatic protons in the Powhatan coal. There is no significant difference between these results indicating that both types of carbons rely on the same set of protons for cross-polarization. These results also indicate that CP/MAS experiments conducted with a pulse delay of ≥ 0.7s should not have intensity distortions due to incomplete ^1H spin-lattice relaxation between successive CP periods.

^{13}C Spin Counting

The large volume MAS system uses Delrin for a large portion of the spinner. Relative to TMS, Delrin has a relatively sharp ^{13}C resonance at 88.8 ppm due to the $(-CH_2-O)_n$ moiety. For most coals, this is a sparsely populated spectral region. Thus, the possibility exists to use the Delrin signed as a "built in" intensity standard for spin counting, or absolute intensity measurements in ^{13}C MAS experiments (8). However, to use Delrin as a built in intensity reference, the

Delrin resonance must first be calibrated using known materials. For these calibrations, various mixtures of hexamethylbenzene (HMB) in MgO were examined in the large-volume Delrin-Zirconia spinner system. On the basis of these experiments, it was determined <u>empirically</u> that the Delrin in <u>the particular spinner used</u> was equivalent to 0.257g HMB, or $6.34 \cdot 10^{19}$ ^{13}C spins in a SP/MAS experiment. Similarly, for a CP/MAS experiment the built in Delrin signal was determined empirically to be equivalent to 0.217g HMB, or $5.41 \cdot 10^{19}$ ^{13}C spins for that particular spinner (8).

Using these "equivalent" spins and the relaxation time data (Table 1), ^{13}C NMR intensities were determined for the SP/MAS and CP/MAS experiments on Powhatan coal (Table 2). The results indicate that the SP/MAS experiment accounts for 90% of the carbons, whereas the CP/MAS experiment accounts for about 49% of the carbons in Powhatan coal. These results are consistent with spin counting results reported by others (1-3).

The spin counting results also show that a greater percentage of the aromatic carbons are detected in the SP experiment, than in the CP experiment. However, the apparent carbon aromaticities for the SP and CP experiments are in reasonable agreement (0.76 versus 0.73 respectively).

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PUBLICATIONS

Zhang, M., and G. E. Maciel. "Large Sample ^{13}C NMR Spectroscopy of Coal. Relaxation and Spin Counting," in preparation.

Zhang, M., and G. E. Maciel. "Delrin as a Built-in ^{13}C Intensity Reference for Solid-State Analysis by Magic-Angle-Spinning Nuclear Magnetic Resonance Spectrometry," in preparation.

Table 1. Relaxation Parameters Derived for Powhatan No. 5 Coal

	Single Pulse[a]		Cross Polarization				
	T_1^C(s)	A	T_1^C(s)	A	T_1^H(MS)[c]	T_{1p}^H(ms)[d]	T_{CH}(ms)[d]
sp^2 Peak							
a)	1.4	0.12	--	--			
b)	8.3	0.39	8.3	0.49	122	6.8	0.30
c)	34.8	0.49	33.3	0.51			
sp^3 Peak							
a)	1.0	0.64	3.4	0.54	130	5.9	0.093
b)	15.1	0.36	15.4	0.46			
Delrin Peak							
a)	0.074	0.28					
b)	2.7	0.24			4.6	80	0.30
c)	9.2	0.48					

[a] Obtained by SP/MAS experiments with t_d = 180 s.
[b] Obtained by CP/MAS experiments with t_d = 0.7 s.
[c] Obtained via ^{13}C intensities, using CP/MAS techniques.
[d] Obtained via variable contact-time CP-MAS experiments.

Table 2. ^{13}C NMR Intensities and Spin Counting Results

Spectrum	Integrated Intensity (M)[a]			Corrected Intensity (M*)[b]			^{13}C Spins x 10 $^{-20}$[c]			Fraction of ^{13}C Detected[d]
	sp^2	sp^3	Delrin	sp^2	sp^3	Delrin	sp^2	sp^3	Total	
Single Pulse	9.43	3.02	1.16	9.43	3.02	1.16	5.15	1.65	6.80	0.90
Cross Polarization	8.38	3.08	1.80	9.70	3.68	1.93	2.72	1.03	3.75	0.49

[a] Integrated intensity taken directly from the spectrum.

[b] Integrated intensity corrected for relaxation effects.

[c] No. of ^{11}3C spins calculated on the basis of the empirical spin-counting calibration referenced to the built-in Delrin signal.

[d] Ratio of the total ^{13}C spins detected to 7.59x10^{20} (the number of ^{13}C spins expected on the basis of classical analytical data).