THE DOUBLE CROSS POLARIZATION ^{13}C-NMR EXPERIMENT IN SOLID FOSSIL FUEL STRUCTURE ANALYSIS

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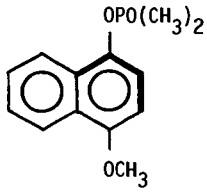
The Double Cross Polarization ^{13}C-MAS/NMR experiment has been used to derive a new operational classification of solid fossil fuels based on chemical reactivity[1,2]. The method requires labeling reactive sites in the organic matrix with a magnetically active isotope not present in the precursor material, and using the local, isolated dipole-dipole interaction between this nucleus and nearby ^{13}C nuclei to detect via cross polarization the carbon centers in the vicinity of the label. The technique is a marriage of chemistry and spectroscopy and the information content of the DCP spectra is defined by both partners.

^{1}H-^{13}C-^{31}P DCP/MAS ^{13}C-NMR spectroscopy has been used to statistically describe phenolic ortho-substitution patterns of coals via their aryl phosphinate or phosphate derivatives, as per model 1. The identification of specific functional group types as the activation source for acidic C-H bonds in these materials has also been effected via the tertiary phosphine oxide derivatives generated from coal carbonions as in model 2. The bold line in these structures indicates the carbon bonding network that is detected by this technique, with signal intensities nominally proportional to the inverse sixth power of the ^{31}P-^{13}C internuclear distance. The sensitive volume element centered on ^{31}P in which DCP signals are observed is determined by the rate at which the ^{31}P-^{13}C cross polarization signal accrues, primarily determined by the depolar interaction strength, and the rate at which this signal decays, the ^{13}C rotating frame T_1. For the ^{31}P-^{13}C pair, DCP signals are confined to a spherical volume element with a ca. 4 A radius.



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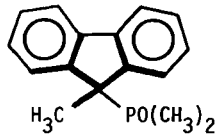

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In these applications of DCP NMR the new, detailed structure and/or reactivity information is realized by detection of carbon resonances one or more bonds removed from the reaction center, but in a volume element of intramolecular dimensions. To the extent that intermolecular contributions to the spectrum are detected, and not recognized as such, the structure/reactivity correlation is weakened.

Direct substitution of phosphorus on the aromatic rings in the organic matrix of the coal is not readily accomplished. This environment potentially can be labeled with fluorine in a selective fashion using newly developed reagents[3]. The possibility of determining the changes in average ring substitution patterns as a function of chemical treatment or coal diagenisis emerges. Recent developments in the field of DCP ^{13}C NMR will be presented.

References

1. Local Structure Evaluation in Solid Organophosphorus Compounds by Double Cross Polarization Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Edward W. Hagaman, submitted for publication.

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3. Singh, S., DesMarteau, D. D., Zuberi, S. S., Witz, M., Huang, H.-N. J. Am. Chem. Soc., 1987, 109, 7194-7196.

Acknowledgement

Research sponsored by the Division of Chemical Sciences/Office of Basic Energy Sciences, US Department of Energy under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.