COAL AND COAL CONSTITUENTS STUDIES BY ADVANCED EMR TECHNIQUES

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ABSTRACT

Advanced magnetic resonance (EMR) methods are used to examine properties of coals, chars, and molecular species related to constituents of coal. During this grant period, further progress was made on proton NMR and low-frequency dynamic nuclear polarization (DNP) to examine the interaction between fluids such as water and the surface of suspended char particles. Effects of char particle size on water nuclear spin relaxation, T₂, were measured.

TABLE OF CONTENTS

Title page	1
Disclaimer	2
Abstract	2
Table of Contents	2
Executive Summary	3
Introduction	3-4
Measurements	4-6
Results, Discussion, and Conclusions	6-7
References	7

EXECUTIVE SUMMARY

The main advanced magnetic resonance methods employed in this project are (1) very low frequency pulsed dynamic nuclear polarization (DNP) spectroscopy for the study of the interfaces between coal-like particles and the water medium in which they are suspended, (2) W-band (100 GHz) electronic magnetic resonance (EMR, EPR, or ESR) spectroscopy to provide an analytical tool to discriminate among very similar chemical species that are constituents of coals and closely related materials such as chars, and (3) a variety of proton nuclear magnetic resonance (NMR) techniques to measure characteristics of the water in contact with the particle surfaces and pore spaces.

As detailed in previous semiannual progress reports to DOE, DNP behavior has revealed a transient chemisorption of water molecules on the external surfaces and/or pore walls of carbon char particles manufactured from particular wood precursors in highly controlled pyrolyses. Previous reports also summarized the use of Fourier Transform Pulsed-Field-Gradient spin-echo NMR spectroscopy to obtain several self-diffusion coefficients in aqueous char suspensions corresponding to different mobilities of water molecules in the porous structures. Proton spin-lattice relaxation data generally confirmed the results of molecular diffusion measurements. It was concluded that the short-range nuclear-electronic interactions in pore space have the dominant effect on DNP enhancement in char suspensions.

The current report describes the first part of a study of NMR relaxation of water protons in char particles suspended in water. A strong particle size influence on NMR transverse proton relaxation in aqueous suspensions of several newly synthesized carbon based chars is found. But the same transverse proton relaxation is nearly independent of the 180° pulse interval in the CPMG NMR pulse sequence. These results are being considered along with other experimental findings and an interpretation will be discussed in the next semiannual report to DOE.

INTRODUCTION

An understanding of intermolecular interactions and molecular motion at the solid-liquid interface is of central importance to research concerning heterogeneous catalysis, fluid penetration of engineering plastics and ceramics, and biological perfusion. Studies of molecular diffusion and relaxation processes in paramagnetic porous materials provide valuable information about surface relaxivity and spin dynamics at the solid-liquid interface [1-2].

Over the past two decades, many different magnetic resonance methods have been used in studies of paramagnetic centers in carbonaceous solids as well as in studies of the surface diffusion of solvents adsorbed on charcoals [2-8]. EPR spectroscopy has shown that unpaired electrons responsible for the paramagnetism of chars exist in stable organic free radicals created during the heat-treatment carbonization [2,3]. Surface diffusion of solvents adsorbed on charcoals already has been the subject of NMR relaxation studies [4-6]. An NMR chemical shift technique also has been applied to study the molecules adsorbed on charcoal and silica gel [7,8]. Self-diffusion coefficients in porous media, measured by different kinds of Pulsed-Field-Gradient

NMR, have been the object of intensive theoretical and experimental studies [9-13]. In spite of significant progress in these studies, the electronic structure of char paramagnetic centers and the process of free radical formation during carbonization, as well as the state of water at the paramagnetic surface, are not yet fully understood. So far, no theoretical calculation related to the electronic structure has been carried out for carbon based chars.

Many reports have shown that the water proton relaxation rate in porous media depends on structural properties, such as porosity, grain and pore size, geometry and distribution, and specific surface interactions, as well as on flow properties, such as permeability, tortuosity and dispersivity [14-17]. Using simple model systems, such as glass beads in water, it was shown that the two-site exchange model can be successfully used to account for relaxation data of solvent protons [15, 17]. However, the origin of enhanced relaxation in real porous structures, as well as the state of water on more complex surfaces, remains a matter of debate. The analysis of relaxation data is especially complicated for aqueous suspensions of paramagnetic porous particles, because water protons are influenced by fast nuclear-electron cross-relaxation on the surface due to hyperfine interactions with the paramagnetic centers in the porous media. Corresponding NMR chemical shifts for molecules adsorbed on the paramagnetic surface usually are obscured by broad resonance line widths. The purpose of this work is to furnish an understanding of molecular diffusion and spin dynamics at the solid-liquid interface in several newly synthesized carbon based chars suspended in water. This report is Part I of this study, providing experimental data that are now being considered and interpreted. The theoretical model will be the basis for Part II, which we hope to present in the next semiannual report to DOE.

MEASUREMENTS

The NMR relaxation measurements were performed at a Larmor ^1H frequency of 6 MHz at room temperature with a relaxometer NMR-07PC, which is a modification of a model previously described [19]. The Carr-Purcell-Meiboom-Gill (CPMG) technique was employed to measure water proton transverse relaxation times with a 180° pulse period, τ , from 10 ms down to 0.2 ms. Special software has been created to account for multi-exponential relaxation, in which the relaxation (echo-decay) curve was described as a sum of several components $A(t)/A(0) = \sum p_i F_i(t)$ with corresponding weighting coefficients p_i . Each component was taken to be exponential: $F_i(t) = \exp(-t/T_{2i})$. To avoid the possible influence of slightly non-exponential time dependencies of $F_i(t)$, only the initial part of each component was used, with consecutive subtraction of the most slowly relaxing $F_i(t)$ -components from the total curve (Fig.1). Relaxation times and relative intensities p_i of components were determined by linear least squares analysis. Data were averaged over 50 acquisitions with phase cycling with a recycle delay of 10 s to avoid saturation. Experimental relaxation time measurement errors did not exceed 5%. High-resolution proton spectra were obtained with a pulsed NMR spectrometer model Tesla-BS-567A, operated at a Larmor ^1H frequency of 100 MHz and equipped with a Fourier transform accessory.

Figure 1. Typical raw CPMG proton spin echo decay data in char suspensions. Spin-echo decay analysis shows the presence of two basic components with different transverse relaxation times, which represent more than 90% of water molecules in the sample.

Samples of chars used in this work were produced by a low-temperature pyrolysis of carbonaceous materials, including hardwood, starch, and fructose, under H_2 flow. Not only do the properties of chars depend upon the nature of the starting material, they also are strongly affected by thermal treatment (both the temperatures and the times of heating) and the gas atmosphere in which the thermal treatment is carried out. The samples were heated at the rate of $10^\circ C$ per hour according to a pre-selected heat treatment profile, with a maximum temperature ranging from 420 - $720^\circ C$. Preparation techniques included digitally programmed temperature profiles, ball milling, and size separation by micro-sieving. Particle sizes from 850 down to $50 \mu m$ were used in these experiments. Samples were ground in an agate mortar to avoid possible orientational effects due to needle shapes. The standard deviation of the particle diameter for any sample was less than 20%. The samples were suspended in water and then bubbled with pure nitrogen for 15 min to reduce the concentration of dissolved oxygen in the solvent. After precipitation for several hours the extra water was removed from the top of the sample. A concentration of $0.82 \pm 10\% \text{ g/cm}^3$ of char particles in suspensions was used. The EPR spectra of chars in water at room temperature consisted of single, nearly Lorentzian lines, with peak-to-peak line widths of about 1.0 G, and a

typical free radical g-factor close to the free electron value of 2.0023. Experimental details of char synthesis are described elsewhere [20,21].

RESULTS, DISCUSSION, and CONCLUSIONS

The chars used in this study have a well-developed porous structure, leading to multi-exponential NMR magnetization decays and several relaxation times. Spin-echo decay analysis shows the presence of two basic components (Fig.1) with different relaxation times which represent more than 90% of all water molecules in the sample. One of them represents 2-9% of water molecules, has comparatively short relaxation times $T_p \approx 3-10$ ms, and demonstrates a weak char particle size dependence. This component (Fig. 1) can be attributed to the water molecules mainly in pore spaces where they are undergoing restricted diffusion and multiple collisions with the paramagnetic walls in a porous cage [22]. High resolution proton NMR usually fails to observe this component. The porous cage effect leads to a slow exchange process between molecules inside and outside the porous structure. Another relaxation component represents 80-85% of water molecules in char suspensions, and has much longer T_2 relaxation times, as well as a strong char particle size dependence (see the Table).

Table. Observed Proton Transverse Relaxation Time $(T_2)_{\text{obsd}, i}$ (in sec) as a Function of 180° Pulse Interval in CPMG Sequence τ in Aqueous Char Suspensions

No.	Char particle size (μm)	τ , ms				
		0.2	1.0	2.0	5.0	10.0
1	850 ± 170	0.743 ± 0.04	0.722 ± 0.04	0.754 ± 0.04	0.741 ± 0.04	0.720 ± 0.04
2	450 ± 90	0.632 ± 0.03	0.624 ± 0.03	0.636 ± 0.03	0.651 ± 0.03	0.648 ± 0.03
3	250 ± 50	0.470 ± 0.02	0.495 ± 0.03	0.467 ± 0.02	0.432 ± 0.02	0.461 ± 0.02
4	100 ± 20	0.208 ± 0.01	0.210 ± 0.01	0.202 ± 0.01	0.213 ± 0.01	0.196 ± 0.01
5	50 ± 10	0.100 ± 0.005	0.087 ± 0.005	0.079 ± 0.004	0.086 ± 0.004	0.086 ± 0.005

For the maximum char particle size ($850 \mu\text{m}$), the ratio between relaxation times of these two components was more than 50. The latter relaxation component can be attributed to the water molecules in the vicinity of the paramagnetic surface. An intense proton NMR line corresponding to this component was observed by high-resolution NMR of char suspensions. Since only one intense NMR line was observed, this indicates that the fast exchange limit applies [23]. It is

speculated that a three-compartment model for exchange may account for these observations. This will be considered further in the next six-month grant period.

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