SOME CURRENT APPLICATIONS OF MAGNETIC RESONANCE IN COAL LIQUEFACTION RESEARCH

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Nuclear magnetic and electron spin resonance (NMR & ESR) spectrometries have proven to be extremely powerful structure-determining tools in coal research (1-4). The techniques have been shown to be especially valuable in studies of coal liquefaction, not only as compositional probes (1-4), but also as means of elucidating reaction mechanisms (4-7). In this paper, the following relatively recent applications of magnetic resonance in coal liquefaction research are described briefly:

- Investigation of the nature of carbon deposits on used coal-liquefaction catalysts
- Determination of the fate of hydrogen during coal liquefaction
- Observation of transient free radicals during coal pyrolysis

The first two of these make extensive use of cross-polarization carbon-13 magnetic resonance combined with magic angle spinning (CP/MAS NMR), whereas the third is an electron spin resonance investigation.

CHARACTERIZATION OF CARBON DEPOSITS ON COAL-LIQUEFACTION CATALYSTS. Coal-liquefaction catalysts are known to be relatively short-lived, especially with regard to sulfur removal (8). Carbon deposition, sintering by steam, and metals deposition are thought to be the principal causes of deactivation (8). The CP/MAS NMR technique is potentially a means of characterizing the carbon deposits.

In a recent cooperative catalyst deactivation study conducted at the Amoco Research Center and the Pittsburgh Energy Technology Center (PETC), selected coal liquefaction catalysts (Table 1) were tested in a continuous reactor for various periods of time. The reactor was operated at 427°C and at 2000 psi H_2. The feed rate of the slurry, which consisted of 25% Illinois No. 6 coal in Koppers Creosote Oil or SRC-II Heavy Distillate, was nominally 400g/hr, and the residence time was approximately 48 minutes.

Representative CP/MAS NMR spectra of catalyst pellets removed from the reactor after 25 and 480 hours of operation are shown in Figure 1. The more intense of the two resonance signals in each spectrum (excluding the aromatic sidebands) is assignable to aromatic carbons; the ratio of the area of this signal to the total spectral area is an indication, if not an absolute measure, of the carbon aromaticity of the carbon deposits on the partially deactivated catalyst samples.

In addition to the CP/MAS measurements, NMR spectra without magic angle spinning, X-ray diffraction patterns, and elemental analyses were obtained for the samples. With increasing time in the reactor, the following occurred:

- The catalyst samples suffered a loss of activity (as measured by conversion to pentane-soluble material).

- The weight percent carbon deposited on the catalysts increased.

- The carbon deposits increased in aromaticity and became more highly ordered.

FATE OF HYDROGEN DURING COAL LIQUEFACTION. A major consideration in the actual operation of any direct coal liquefaction process is the price paid for hydrogen comsumed during the process. To better understand the fate of this hydrogen, PETC is developing a method to determine the amount of hydrogen consumed via the following (7):

- Hydrogenation

- Hydrogenolysis to produce light hydrocarbon gases

- Hydrogenolysis of C-C bonds resulting in breakdown of the coal matrix

- Heteroatom elimination

The method requires the use of elemental analysis, NMR data, and an accurate carbon mass balance (including gases), together with several assumptions concerning the stoichiometry of the four classes of reactions given above. The model leads to the relationship

$$\Delta H = \Delta f_a + 2\Delta C\text{-}C + \Delta NOS$$

in which the numerical data are scaled to 100 carbon atoms of total feed. In the equation, ΔH is the total number of hydrogens incorporated into carbonaceous products, Δf_a is the number of carbons hydrogenated, ΔNOS is the number of heteroatoms removed, and $\Delta C\text{-}C$ is the number of C-C bonds broken via hydrogenolysis. Three of the four terms in the equation can be readily deduced from experimental data; $\Delta C\text{-}C$, however, is determined by difference. Knowledge of the gas make and composition allows separation of the $\Delta C\text{-}C$ term into a gas make contribution and a matrix bond contribution. The results of applying the method to an experimental run in the PETC 400 lb/day coal liquefaction PDU are given in Table 2. Note that approximately half the hydrogen consumed during the run is involved in C-C bond breaking mechanisms.

OBSERVATION OF TRANSIENT RADICALS DURING COAL PYROLYSIS. Although much evidence exists that suggests free radical mechanisms are operative in coal liquefaction processes (9-11), free radical intermediates have never been directly observed during such processes. Recent high-pressure, high-temperature ESR studies under simulated coal liquefaction conditions have provided considerable insight into experimental factors affecting liquefaction behavior (5); nevertheless, transient radicals were not detected. This leads one to speculate that any radicals formed during the initial thermolysis react readily with hydrogen donors. In the present work, we have observed the behavior of the free radicals in coal during rapid pyrolysis directly in the cavity of an ESR spectrometer. Two versions of the *in situ* ESR pyrolysis experiments were conducted. In the first version, the sealed ESR sample tube was completely within the high temperature region of the cavity; in the second version, several centimeters of the sample tube extended outside the cavity into the ambient air.

In that version of the experiment in which the sample was completely immersed in the heated zone of the cavity, Ireland Mine coal heat-treated at 535°C showed a rapid increase in free radical content; within five minutes after the pyrolysis

had begun, the number of free radicals had increased by a factor of approximately three. The pyrolysis experiments were then repeated in the presence of 9,10-dihydroanthracene -- a known hydrogen donor -- and in the presence of phenanthrene -- a nondonor. The free radical concentration per gram of coal was found to be independent of the presence of phenanthrene; however fewer radicals per gram of coal were formed during pyrolysis in 9,10-dihydroanthracene. These results are consistent with current theories of coal liquefaction. The pyrolysis of coal, either alone or in the presence of a nondonor solvent, results in the formation of free radicals, which tend to recombine into relatively high-molecular-weight products. Pyrolysis in the presence of a donor solvent, however, results in a more efficient capping of these radicals by the donatable hydrogen or by small radical fragments from the solvent.

The fact that no transient radicals were observed suggested that the lifetimes of the radicals were simply too short to permit the accumulation of a population large enough to be detected in an ESR experiment. A possible explanation for this behavior is that primary tars formed during the pyrolysis of coal acted as a donor solvent similarly to, but not as efficiently as, the 9,10-dihydroanthracene. A possible way to explore this hypothesis would be to allow the tars to be removed from the reaction zone of the coal.

This was accomplished by using the second version of the ESR pyrolysis experiment in which part of the sample tube extended into a "cold" zone, i.e., ambient air, outside the heated portion of the cavity. The rapid heating of the sample produced a transient population of unstable free radicals, which reached a maximum after approximately two minutes of pyrolysis at 535°C (Figure 2). In addition to the transient radicals, a population of free radicals in excess of the population present in the original coal was produced. Pyrolysis at 510°C and at 495°C produced similar behavior, although the population maxima were not nearly so pronounced as the maximum produced at 535°C and occurred after a longer period of reaction time. Pyrolysis at 495°C produced a slight excess population of stable free radicals with only slight evidence of a transient population. Extrapolation of the time-dependent populations at the three temperatures to zero pyrolysis time resulted in a population somewhat greater than that observed for the coal itself. The apparent g value, after an initial small downward shift, was constant during pyrolysis at all temperatures and suggested carbon-centered radicals. The spectral linewidths, measured as full width at half intensity of the absorption peaks, reached a maximum value at about the same time the population reached a maximum.

The presence of a maximum in the spin population vs. time curve implies that there is more than one step in the mechanism that produces the stable free radical species. It also shows that reactive free radicals are formed during pyrolysis at temperatures only slightly higher than those commonly used in coal liquefaction processes. The presence of a resonance linewidth in excess of that observed for either the coal or the coal after extended periods of heat treatment implies either that a chemically heterogeneous population of radicals is present during pyrolysis or that the radical centers on the transient species are richer in hydrogen than the centers on the stable radicals. The rather constant g value indicates that the latter choice is the correct one, as it seems unlikely that a new heterogeneous population of transient radicals would have an average g value within one ppm of the average observed for the heat-treated coal. The initial small shift toward a lower g value has been observed at much lower temperatures and may be ascribed to loss of oxygen as CO, CO_2, and H_2O (6).

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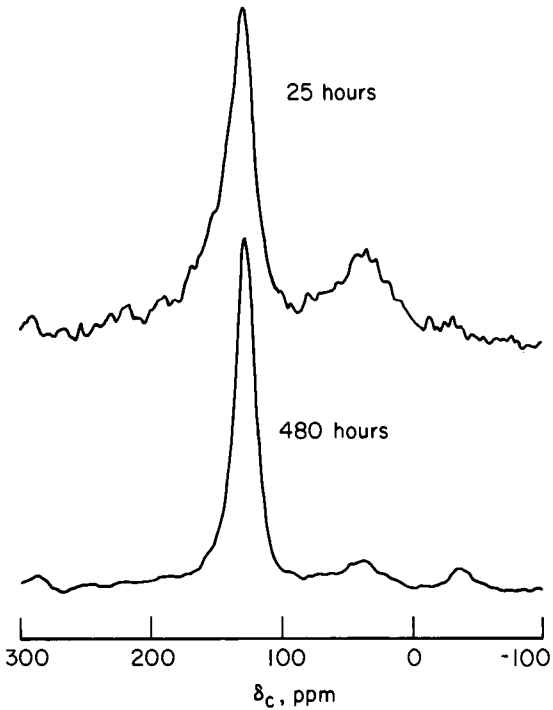

Figure 1.-CP/MAS ^{13}C NMR spectra of aged Amocat 1A catalysts.

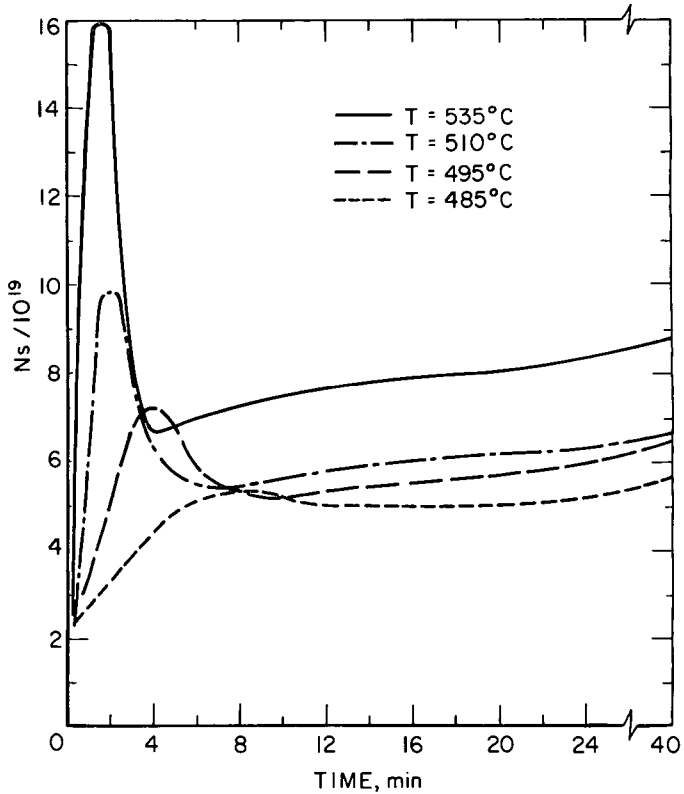

Figure 2.-Free radical formation during rapid pyrolysis of Ireland Mine coal.

Table 1. Catalyst Specifications

Chemical Composition	*Amocat 1A*	*1442A*
MoO_3, wt% on dry basis	16.0	
CoO, wt% on dry basis	3.0	
Surface Properties		
BET surface area, m^2/g	170 minimum	332
Average micropore diameter, Å (determined by N_2 sorption)	120 ± 10	56
Total pore volume, cm^3/g (determined by N_2 sorption and Hg porosimetry)	0.75 ± 0.05	0.74
% Pore volume in macropores (determined by N_2 sorption and Hg porosimetry)	18 ± 5	28

Table 2. The fate of hydrogen consumed in Run FB-62

Reaction	*Hydrogens / 100 C*	*%Hydrogen Consumed*
Hydrogenation	3	30%
C-C Linkage Breaking		
To generate light gas	2	20%
To break down matrix	3	30%
Heteroatom Elimination	2	20%
Total	10	100%