

POSTER

SOLID STATE ^{13}C NMR CHARACTERISATION OF PARTIALLY CARBONISED PITCHES AND COALS

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INTRODUCTION

The determination of aromatic, aliphatic and other carbon group concentrations will improve our understanding of the thermal transformations that occur during carbonisation of pitches and coals. Over the past decade, solid state ^{13}C NMR spectroscopy has made a considerable impact on the characterisation of carbonaceous materials since, in principle, it is the only analytical technique that enables the direct quantitative determination on the carbon types present ⁽¹⁾. The use of the well-established techniques of high power decoupling, magic angle spinning (MAS) and cross-polarisation (CP) allows to obtain high resolution ^{13}C spectra on a routine basis. However, due to unfortunate spin dynamics in CP, not all the carbons are observed by this technique and concentrations of non-protonated aromatic carbons are usually underestimated ^(2,3). It has now been established that the best strategy to obtain quantitative ^{13}C NMR results on coals and their derivatives is offered by a combination of a low magnetic field strength to avoid problems with spinning sidebands and the simple, albeit insensitive, Bloch decay or single pulse excitation (SPE) technique ^(2,3). Only CP has thus far been applied to carbonised samples ⁽⁴⁾.

In this study, the SPE technique has been used to follow bulk chemical transformations of coals and pitches during carbonisation. A suite of partially carbonised samples obtained from the Juranek furnace for a coking coal have been characterised. Further, the structures of thermally treated pitches and their toluene-insoluble (TI) fractions have been determined as part of a study to improve the quality of pitch for increasing the extent of mesophase formation in relation to the production of high performance carbons.

EXPERIMENTAL

The series of partially carbonised coals (PCC) for investigation were prepared from the carbonised block obtained from the Australian bituminous coal. A device was designed to dissect 0.15 cm thick fractions covering the temperature range 325-625°C. The toluene insoluble pitch fractions studied (CTP/TI) were obtained from a coal tar pitch preheated between 250-380°C and under vacuum (80-125 mm. Hg). All the ^{13}C NMR studies were carried out at 25 MHz on a Bruker MSL100 spectrometer with MAS at 5.0 kHz as described

previously ^(2,3) to give spectra in which the sidebands intensities are only α 7% of the central aromatic bands. The ^1H decoupling and spin-lock was ca 60 kHz. As in earlier work ^(2,3), tetrakis(trimethylsilyl)-silane (TKS) was used as an internal standard to determine the proportion of carbon observed. For purposes of comparison, CP spectra were also obtained. In addition, ^{13}C thermal relaxation times (T_1 s) were determined to ascertain the recycle delay of 5 times the ^{13}C T_1 required in the SPE experiments. Dipolar dephasing (DD) CP and SPE measurements were carried out in order to determine the proportions of non-protonated aromatic and bridgehead aromatic carbons (C_{br} , as a fraction of the total aromatic carbon).

RESULTS AND DISCUSSION

Table 1 lists the carbon skeletal parameters and the ^{13}C thermal relaxation times for a selection of the samples studied. Figure 1 shows the SPE spectra for the parent coal and the PCC samples at 411 and 612°C. The concentrations of bridgehead aromatic carbon (Table 1) have been estimated from the total concentrations of non-protonated aromatic carbon by assuming (i) that between 70 and 100% of the aliphatic carbon is adjacent to aromatic rings and (ii) that phenolic oxygen accounts for over half of the total oxygen contents determined by difference from elemental analysis. As for the initial coal, virtually all of the carbon has been observed by SPE for the PCC samples and the aromaticity values are higher than those estimated by CP (Table 1). The concentrations of unpaired electrons are undoubtedly higher in the partially carbonised samples, as reflected by both the ^{13}C T_1 s falling with increasing temperature (Table 1). However, the concentrations are not sufficiently high to result in significant amounts of the carbon becoming undetectable by SPE. Indeed, the shorter ^{13}C T_1 s make SPE a much more efficient approach for low temperature chars than for coals.

Heating the coal to 350°C and the subsequent onset of fluidity is accompanied by relatively small increases in aromaticity and bridgehead aromatic carbon concentration which could well be associated with the loss of volatiles. During the fluid stage (α 350-470°C, PCC 1, Table 1), the aromaticity again only increases slightly, but there is a more noticeable increase in the bridgehead aromatic carbon concentration. When resolidification occurs (α 450°C, PCC2 and 3), there is a large increase in both

overall aromaticity and bridgehead aromatic carbon concentration, corresponding to the growth of aromatic ring systems from α 10-12 to 15-20 rings. Table 1 lists the aromaticities and bridgehead carbon derived from SPE spectra for two of the pitch fractions investigated. As there is little aliphatic carbon and oxygen in the CTP/TI samples, the errors involved in deducing the bridgehead aromatic carbon concentrations (C_{br}) are relatively small. Figure 2 compares the aromaticity carbon intensity plots obtained from DD using SPE and CP with a 1 ms contact time. As for coals, over 90% of the carbon was observed by SPE in the TI fractions of the coal tar pitch. CP again tends to underestimate non-protonated aromatic carbon concentration (Table 1). The results obtained indicate that the average size of the aromatic nuclei corresponds to 15-20 rings peri-condensed structure for the TI fractions.

CONCLUSION

The results have demonstrated the value of the quantitative SPE ^{13}C NMR methodology for providing structural parameters to understand the chemical transformations that occur during the carbonisation of both coal and pitch.

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Table 1. Carbon structural parameters and ^{13}C thermal relaxation times.

| Sample | Temp./ °C | f_a (± 0.01) ^a | $f_{\text{non-pro}}$ (± 0.02) | C_{br} ^b (± 0.04) | ^{13}C T_1 /s |
|-----------------------|-----------|-----------------------------------|-------------------------------------|--------------------------------------|--------------------------|
| Coal | -- | 0.87 (0.76) | 0.62 (0.62) | 0.45 | 16.3 |
| PCC-1 | 411 | 0.90 (0.78) | 0.70 (0.63) | 0.56 | 9.3 |
| PCC-2 | 468 | 0.97 (0.85) | 0.71 (0.69) | 0.66 | 3.0 |
| PCC-3 | 612 | 0.99 (0.99) | 0.74 (0.69) | 0.71 | 1.2 |
| CTP/TI-1 ^c | 250 | 0.99 (0.99) | 0.61 (0.64) | 0.58 | 15 |
| CTP/TI-2 ^d | 370 | 0.99 (0.99) | 0.61 (0.58) | 0.57 | 10 |

a The values in brackets were determined by CP.

b Bridgehead aromatic carbon expressed as fraction of total aromatic carbon.

c Derived from a CTP containing 12% w/w TIs.

d Derived from CTP containing 456% TIs.

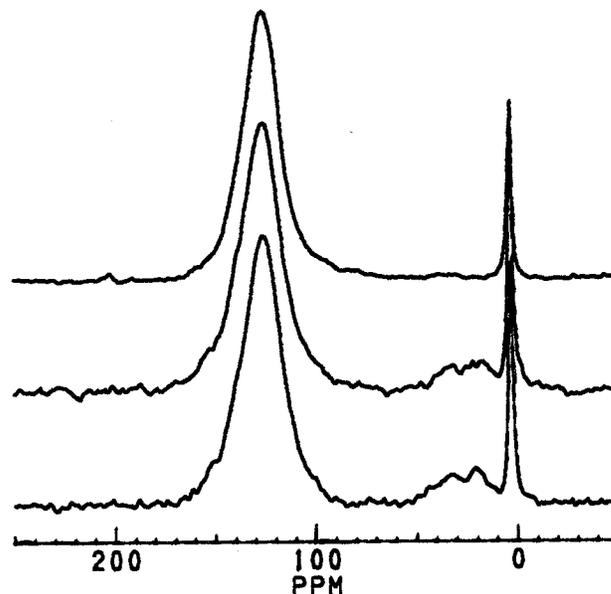


Figure 1. SPE ^{13}C NMR spectra for the initial coal (bottom) and the 411 (middle) and 612°C (top) partially carbonised samples.

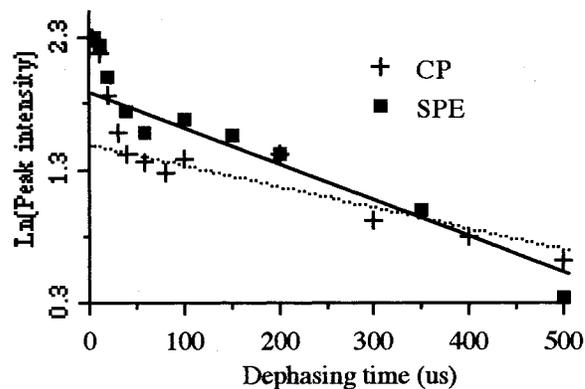


Figure 2. Comparison of aromatic peak intensities from the SPE and CP (1 ms contact time) dipolar dephasing experiments on the toluene insoluble fraction from CTP1.