ELSEVIER

Catalysis Today 37 (1997) 285–293

CATALYSIS TODAY

Structural characterisation of catalytic coke by solid-state ^{13}C-NMR spectroscopy

Colin E. Snape*, Brian J. McGhee, Shona C. Martin, John M. Andresen

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK

Abstract

After reviewing some recent studies on the characterisation of coke deposits on fluid catalytic cracking (FCC) and hydroprocessing catalysts by solid state ^{13}C-NMR, the quantitative structural information that has been obtained through the use of demineralisation of FCC catalysts to provide coke concentrates for analysis will be described. The deactivated catalysts investigated contain only approx. 1% (w/w) carbon and were obtained both from refinery units operating with heavy feeds and from laboratory fluidised-bed tests with *n*-hexadecane. As for other carbonaceous materials, the use of a low-field field strength in conjunction with the single pulse excitation (SPE or Bloch decay) technique has enabled most of the carbon to be detected and, therefore, NMR-invisible graphitic layers are not thought to be major structural features of the cokes. Although stripping the catalysts gives rise to highly aromatic cokes (aromaticity>0.95), even for *n*-hexadecane, differences in feedstock composition are still reflected in the structure of the resultant cokes with those derived from *n*-hexadecane containing less condensed aromatic nuclei than those from heavy feeds.

Keywords: Catalytic coke; Catalytic cracking; NMR

1. Introduction

Deactivation via coke deposition affects all hydrocarbon conversion catalysts with the timescale for this ubiquitous phenomenon varying from just a few seconds for fluid catalytic cracking (FCC) using heavy petroleum feeds (vacuum gas oils and atmospheric residues, B.Pt.>approx. 350°C) to several months for naphtha reforming. Information is needed on both the spatial distribution within catalyst pores and the bulk composition of catalytic coke to gain an overall picture of coke formation and help to best optimise strategies for catalyst regeneration and replacement. For example, in FCC, the coke selectivity can markedly affect a unit's profitability since the catalyst acts as a heat-transfer medium with the heat liberated by coke combustion providing the energy for the endothermic cracking reactions. The economic importance of catalyst deactivation has meant that coke deposition, particularly for hydroprocessing and FCC catalysts, has been the subject of much investigation [1–4]. However, there is still a lack of detailed mechanistic knowledge on coke formation, largely due to the problems associated with the structural characterisation of the insoluble organic matter present in relatively low concentrations on hydrocarbon conversion catalysts (approx. <15% (w/w)).

In principle, of all the spectroscopic techniques (FTIR, mass spectrometry, etc.) available to probe the organic structure of catalytic coke deposits that

*Corresponding author.

PII S0920-5861(97)00021-7

are insoluble in common organic solvents, solid-state ^{13}C-NMR has the unique ability to directly determine the distribution of aromatic, aliphatic and other carbon types present. High-resolution ^{13}C-NMR spectra of coals, oil shales and other carbonaceous materials can be obtained routinely [5–7] using the well-established techniques of high power decoupling, magic-angle spinning (MAS) to remove chemical shift anisotropy (approx. 100 ppm for aromatic carbons) and cross-polarisation (CP) in which magnetisation is transferred from abundant ^{1}H to dilute ^{13}C spins to improve sensitivity and so avoiding long relaxation delays. Further, the introduction of a short relaxation (dephasing) period with the decoupler switched off into the standard CP sequence allows spectra containing peaks from non-protonated aromatic carbons and rotationally mobile aliphatic carbons, principally CH_3 and long-chain CH_2 to be obtained. However, there has been considerable doubt concerning the quantitative reliability of aromaticity and other structural parameter measurements. Not all of the carbon in coals is observed by CP [8] (only approx. 50% for coals) due to the unfortunate spin dynamics which usually discriminates against aromatic carbon. Further, problems are posed by high magnetic field strengths because either special pulse sequences or extremely high MAS speeds are needed to remove spinning sidebands arising from the incomplete removal of chemical shift anisotropy.

These factors, coupled with the inherent insensitivity of the technique have posed considerable problems for the characterisation of catalytic coke. Indeed, there is a general consensus that the use of low field strengths with Bloch decay or single pulse excitation (SPE) offers the best compromise for quantitative ^{13}C-NMR analysis of coals and solid fuels [8–11], albeit with a considerable sacrifice in sensitivity since long recycle times (with 90° pulses, five times the ^{13}C thermal relaxation times (T_1)) are required to ensure that the ^{13}C magnetisation fully regains equilibrium. In principle, the only carbon not observable is that in the vicinity of paramagnetic centres which obviously include graphite. To apply this methodology successfully to deactivated catalysts, the aluminosilicate matrices must first be demineralised to provide coke concentrates in quantities of at least 100 mg. This article first reviews some recent investigations characterising coke deposits on hydroprocessing and FCC catalysts by solid-state ^{13}C-NMR [12–18] before going on to describe the precise carbon skeletal information that has been obtained by using demineralisation to provide coke concentrates for analysis [19–21]. In some of the investigations reviewed, supporting information has been obtained by other techniques, such as FTIR [13] and pyrolysis-MS [19,20]. While these techniques can identify general trends, they are no substitute for ^{13}C-NMR if carbon skeletal information on catalytic coke is required. Although this article deals exclusively with the use of ^{13}C-NMR to elucidate the structure of catalytic coke, ^{129}Xe-NMR has become an extremely powerful technique for probing the spatial distribution of coke within zeolite channels [14,22] through its ability to differentiate between xenon undergoing (i) interactions with strong cationic sites, (ii) normal cavity wall interactions and (iii) collisions with other xenon atoms in the micropore volume.

2. Previous studies

2.1. FCC

Fundamental deactivation studies involving NMR on zeolites thus far have generally involved high concentrations of coke in relation to normal FCC operation where catalysts are regenerated typically after only approx. 1% (w/w) of carbon has been deposited. The high concentrations have been necessary to achieve sufficient sensitivity for characterising the coke on the deactivated catalysts by solid-state ^{13}C-NMR. Further, investigations thus far have concentrated on small molecules (e.g., ethene, *n*-hexene and propylbenzene) [12–14] where coke formation will be initiated from within the framework for zeolites with relatively large pores, such as ultra-stable type Y (USY). Such investigations have the advantage of being able to identify intermediate species involved in the formation of insoluble coke.

Groten et al. [12] investigated coke formation on zeolite USHY with 1-hexene as the feed. They found that the irreversibly adsorbed surface species comprised both aromatic and aliphatic species at the lower reaction temperature of 305°C used. After the coke concentration had reached a steady state of approx. 6% (w/w), ^{13}C-NMR indicated that there was little

variation in the coke structure. Methyl groups dominated in the aliphatic region of the spectra, consistent with the highly substituted acyclic mono-alkenes identified in the liquid product. A minor resonance at approx. 2 ppm was assigned to aliphatic carbons shielded by their orientation to aromatic ring systems in the coke.

Lange and coworkers [13] used ^{13}C-enriched ethene to follow the formation of polyaromatic structures on H-mordenite. After adsorption at ambient temperature, ethene polymerised to linear and branched alkanes which then cracked upon heating to 227°C where the ^{13}C-NMR spectra of the adsorbed species indicated the presence of alkyl, allyl and aromatic carbons, together with allyl and alkyl carbocations. It was also observed that the aromatic band at 1600 cm^{-1} in the IR spectrum that was assigned to coke appeared at this temperature with a decrease in the characteristic paraffinic bands. Although adsorbed hydrocarbons (propane, *n*- and *iso*-butane) were identified on dealuminated H-mordenite at 427°C, the coke was highly aromatic in character. Supporting evidence was again provided by IR spectroscopy where a weak band at 3080 cm^{-1} indicative of the C–H stretch of aromatics was observed with no evidence of paraffinic species.

Liu et al. [14] characterised the coke formed from cracking propylbenzene at 200°C and 280°C on USY and ZSM-5 zeolites. On USY, ^{129}Xe-NMR indicated that the coke had formed within the supercages and the CP ^{13}C-NMR spectra showed that the coke was highly aromatic. In contrast, on ZSM-5, the coke possessed considerable alkyl character and was formed at the channel openings. However, vacuum treatment at 450°C resulted in the aliphatic carbon peaks disappearing from the ^{13}C-NMR spectra which suggests that the alkyl species are molecular in character rather than being part of any insoluble coke that might have formed.

2.2. *Hydroprocessing*

Deactivated Ni/Mo and Co/Mo γ-alumina-supported catalysts have also been characterised in a number of studies by solid-state ^{13}C-NMR [15–18] where coke levels are generally higher (aprrox. 5–15% (w/w)) than on cracking catalysts. Egiebor et al. [15] observed that the aromaticities of coke on hydroprocessing catalysts varied considerably, depending on the nature of the feed and the position of the catalyst in a series of hydrotreating reactors. Different feedstocks and operating conditions formed carbonaceous deposits with aromaticities (proportion of aromatic carbon of the total carbon) ranging from 0.38 for a gas oil to 0.91 for a bitumen. The aromaticity of the coke increased with severity for a given feed, but showed no correlation with those of the different feeds used. Yoshimura et al. [16] also observed relatively low aromaticities in deposits on spent Co/Mo catalysts from the hydrotreatment of coal liquids and attributed the presence of the significant aliphatic carbon content to adsorption of toluene-insoluble compounds. Zeuthen et al. [17] found that the aromaticity of the coke obtained from hydroprocessing a gas oil was low whilst that from a resid under more severe conditions was much higher. Although, in these studies, it is likely that CP has failed to observe much of the carbon resulting in the aromaticities being underestimated, the technique nonetheless highlights instances where significant variations in coke structure do exist.

To investigate quantitative aspects of ^{13}C-NMR analysis of coke deposited on a typical hydroprocessing catalyst, Fonseca et al. [18] analysed mixtures of pyrene and cholestane in their initial adsorbed state and after artificial coking at 400°C. Although "depth" pulses had to be used to remove background signals from the probe, quantitative results were obtained for the intial pyrene/cholestane mixtures using the SPE technique. However, for the coked samples which were generally highly aromatic in character, even for cholestane, between 30% and 70% of the carbon was invisible. The missing carbon was ascribed to graphitic structures [18] although much higher temperatures are normally required for the formation of large aromatic domains. It is more likely that paramagnetic centres on relatively small aromatic nuclei (a few rings) has resulted in the carbon being broadened to such an extent that is no longer observable.

3. FCC coke concentrates

3.1. *Background*

The aim of our recent studies [19–21] has been to demonstrate (i) that it is possible to characterise catalytic coke at concentrations of approx. 1% (w/w)

that are typically encountered in normal FCC operations and (ii) to what extent the structure of the coke is affected by feedstock composition and the extent of stripping. The investigation on *n*-hexadecane-derived coke extends our earlier studies on the roles of quinoline, phenanthrene and other model compounds as poisons and coke inducers for *n*-hexadecane [23,24].

3.2. *FCC catalysts and their demineralisation*

The FCC catalysts used were typical commercial formulations and the deactivated refinery samples were obtained from units processing two heavy feedstocks, namely a heavy residue feedstock (approx. 1.5% sulphur, a Conradson carbon content of 5.0% (w/w) and Ni and V) and a hydrogenated vacuum gas oil (HVGO) [19,20]. To determine how the yields and composition coke vary in FCC as a function of stripper conditions [21], tests have been conducted in a fluidised-bed reactor using *n*-hexadecane at 520°C, a commercial FCC catalyst with a stripping period of 120 min. The all-silica laboratory-scale fluidised-bed reactor used had a 4-cm diameter bed and, during each run, approx. 30 g *n*-hexadecane was fed into the reactor containing 80 g of catalyst.

The deactivated FCC catalysts all had carbon contents close to 1%. They were first refluxed in chloroform for 3 h to remove any entrained molecular species and then vacuum-dried prior to demineralisation. The cokes were then concentrated by applying the standard demineralisation procedure for solid fuels [22] to the chloroform-extracted catalysts. This involved successive extraction with 2 M hydrochloric acid (stirring overnight at 60°C) and 40% hydrofluoric acid (HF), the HCl-extracted sample being stirred at room temperature for 4 h with 20 cm^3 of HF being used per gram of sample. The coke concentrates were finally washed with dilute hydrochloric acid to remove any remaining inorganic paramagnetics prior to collection in plastic filtration equipment. The coke concentrates had carbon contents in the range 30–60% (w/w).

3.3. ^{13}C-NMR *analysis*

CP and SPE ^{13}C-NMR measurements on the coke concentrates were carried out as previously described [10,19,20] at 25 MHz using a Bruker MSL100 spectrometer with magic-angle spinning (MAS) at 4.5–5.0 kHz to give spectra in which the sideband intensities are only approx. 3% of the central aromatic bands. Approximately approx. 150 mg of sample was packed into the zirconia rotors. The ^{1}H decoupling and spin-lock field was approx. 60 kHz and, for SPE, the 90° ^{13}C pulse width was 3.4 ms. A recycle delay of 50 s was employed between successive 90° pulses in SPE to ensure that virtually thermal relaxation occurred. Normal CP spectra of the coke concentrates were obtained using contact times of either 1 or 5 ms. Dipolar dephasing (DD) was combined with both SPE and CP to estimate the proportion of protonated and non-protonated aromatic carbon using a dephasing period of 50 μs. No background signal was evident in the SPE spectra from the Kel-F rotor caps. The measurement of aromatic and aliphatic peak areas manually was found to be generally more precise than using the integrals generated by the spectrometer software.

3.4. *Quantitative aspects*

Figs. 1 and 2 compare the CP and SPE ^{13}C spectra of the highly aromatic refinery coke concentrates and Fig. 3 presents the decays of the aromatic peak intensities in the CP and SPE-DD experiments on the residue-derived coke. The carbon skeletal parameters obtained from the SPE and CP ^{13}C-NMR experiments for both samples are summarised in Table 1. The sensitivity is obviously superior in the CP spectra (7–10 000 scans for CP compared to 1000–2000 for SPE, Figs. 1 and 2) but, as found for many coals [9–11], CP significantly underestimates the carbon aromaticity using relatively short contact times (Table 1, CP values for 1 ms contact, estimated error±0.01). This arises from the non-protonated aromatic carbons, in particular, cross polarising much more slowly than the aliphatic carbons. At longer contact times, the discrimination against aromatic carbon is not quite as acute, but the aromaticity values obtained are still slightly lower than that by SPE (Fig. 4). This is indicative that some aromatic carbon, presumed to be in the vicinity of free radicals, is not polarised at all. The fact that 70% and 90% of the carbon in the residue and HVGO-derived coke concentrates, respectively, was observed by SPE demonstrates that the procedure is reasonably quantititive

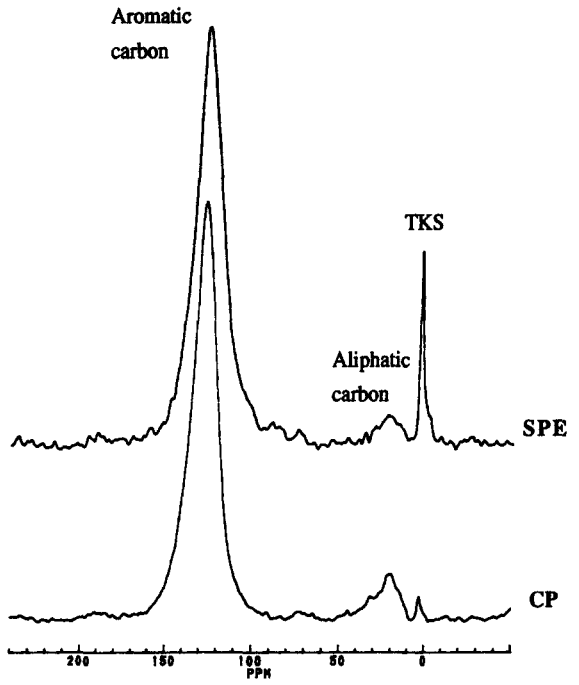

Fig. 1. CP (1 ms contact time) and SPE ^{13}C spectra of the coke concentrate from FCC refinery catalyst deactivated using a residue feedstock.

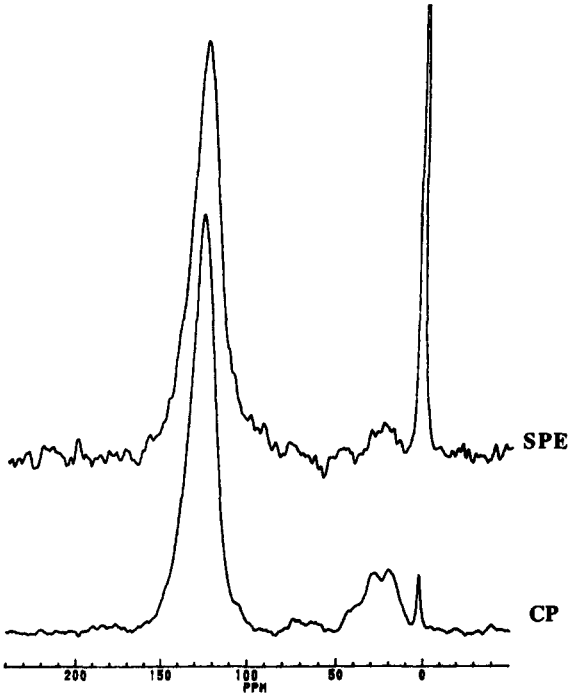

Fig. 2. CP (1 ms contact time) and SPE ^{13}C spectra of the coke concentrate from FCC refinery catalyst deactivated using a HVGO feedstock.

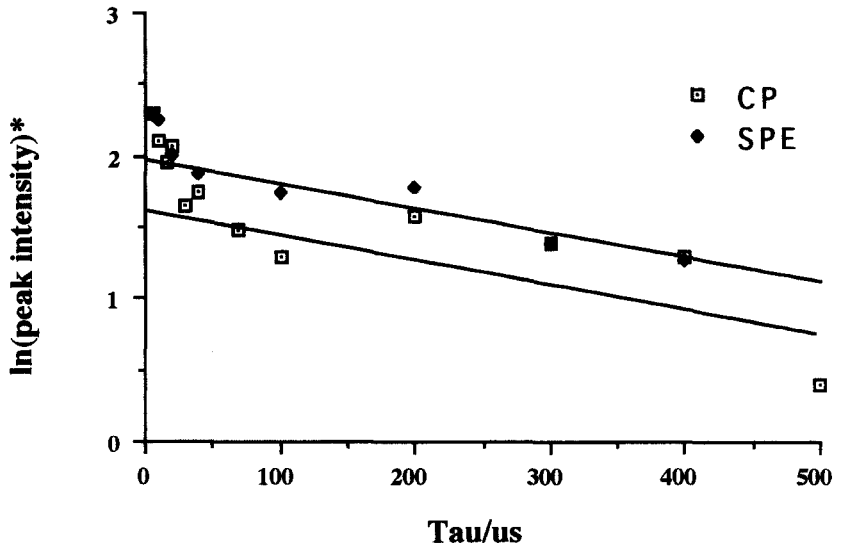

Fig. 3. Decay of the natural logarithm of the aromatic peak intensity in the CP and SPE diploar dephasing experiments on the coke concentrate from FCC catalyst deactivated using the residue feedstock (initial intensity assigned value of 10).

Table 1
Summary of carbon skeletal parameters for the coke concentrates

Parameter	Sample			
	Residue	HVGO	*n*-Hexadecane	
			Initial	Stripped
Aromaticity, f_a (±0.01)[a]				
CP (1 ms)	0.91	0.85	0.82[c]	ND
SPE	0.97	0.96	0.83[c]	0.92
Fraction of aromatic carbon that is non-protonated (±0.02)[a]				
CP (1 ms)	0.55	ND	ND	ND
SPE	0.67	0.56	0.55	0.50
Fraction of aromatic carbon that is bridgehead, C_{BR}/C_{AR} (SPE, ±0.03)[b]	0.63	0.51	0.40	0.45
Fraction of aliphatic carbon that is CH_3 (10–24 ppm range, SPE)	0.75	0.50	0.30	0.75
Carbon observed by SPE (%)	70	90	ND	ND

ND=not determined, SPE=single pulse excitation, CP=cross-polarisation.
[a]Estimated errors.
[b]Average value for protonated and non-protonated carbons.
[c]Not including carboxyl and carbonyl.

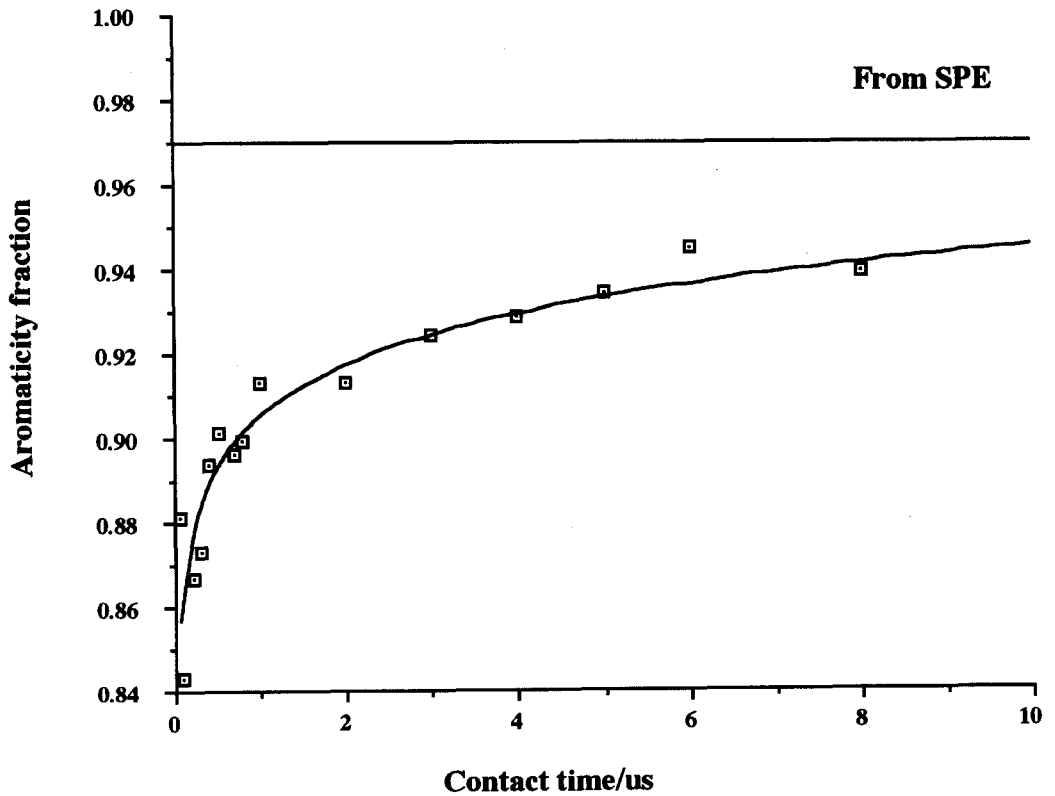

Fig. 4. Variation of aromaticity as a function of contact time in CP for the coke concentrate from FCC catalyst deactivated using the residue feedstock.

and that graphitic layers cannot be present in large concentrations.

As for the total aromaticity, CP also grossly underestimates the fraction of non-protonated aromatic carbon determined by dipolar dephasing (Table 1, estimated error±0.02). This can be seen in the decay of the aromatic peak intensity (Fig. 3); the faster relaxing Gaussian component for the protonated aromatic carbon has virtually decayed completely after approx. 60 μs with the slower relaxing exponential component from the non-protonated carbon having a time constant of over 500 μs. After the intial decay of the protonated aromatic carbon, the intensity of the remaining non-protonated carbon is modulated by the rotation of the rotor at 5 kHz, this effect being particularly evident in Fig. 3 for the CP experiment (note that this modulation is not encountered in variable contact time CP measurements due to the much longer timescale).

3.5. *Structure of the refinery cokes*

From the fractions of non-protonated aromatic carbon derived by SPE (Table 1), it is estimated that bridgehead aromatic carbons (C_{BR}/C_{AR}) account for approx. 67% and 56% of the total aromatic carbon in the residue and HVGO-derived cokes, respectively. The only assumptions needed are that (i) each aliphatic carbon is bound to one aromatic carbon, which is not unreasonable in light of the distribution of aliphatic carbon (see later) and (ii) the concentrations of heteroatoms in the cokes are relatively small (total concentration corresponding to less than approx. 2 mol% carbon). If peri-condensed aromatic structures are drawn to fit the C_{BR}/C_{AR} values (Table 1), 15–20 rings are required for the residue feedstock coke compared to only 8–12 rings for the HVGO sample. This represents a significant difference in aromatic structure which is considered to arise primarily from the major differences in feedstock composition and, along with other factors, particularly the Ni and V concentrations, could well affect combustion behaviour in the regenerator.

Although in the refinery the cokes are clearly highly aromatic in character, some information on the distribution of aliphatic groups can also be obtained from the ^{13}C-NMR spectra. Intuitively, one would expect virtually all the aliphatic carbon to be adjacent to aromatic rings in either arylmethyl or diarylmethylene groups. The fraction of aliphatic carbon present as methyl has been estimated from the intensity of the 10–24 ppm chemical shift range (Table 1, a fairly clear separation between CH_2 and CH_3 chemical shifts for the aliphatic structures in high-rank coals occurs at 23–24 ppm). The SPE spectrum (Fig. 1) suggests that arylmethyl groups account for approx. 75% of the aliphatic carbon in the residue-derived coke (Table 1). Although the signal to noise levels of the aliphatic bands are not good, this fraction appears to be much higher than for the HVGO-derived coke where CH_3 accounts for approximately only half of the aliphatic carbon (Fig. 2 and Table 1). The larger proportion of CH_2 (and CH if present) in the HVGO-derived coke is again consistent with the differences in composition between the two feedstocks. By definition, the more aliphatic HVGO contains higher concentrations of both long chain alkyl and naphthenic moieties than the more aromatic residue.

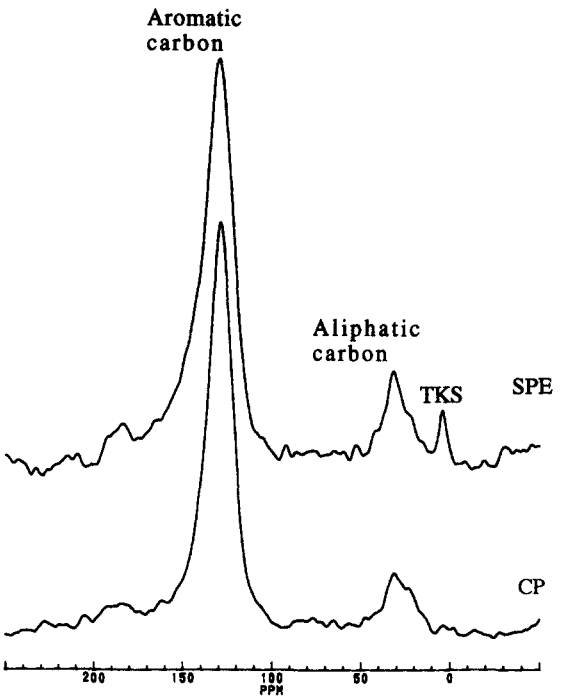

Fig. 5. CP (1 ms contact time) and SPE ^{13}C-NMR spectra of the coke concentrate obtained from *n*-hexadecane without stripping.

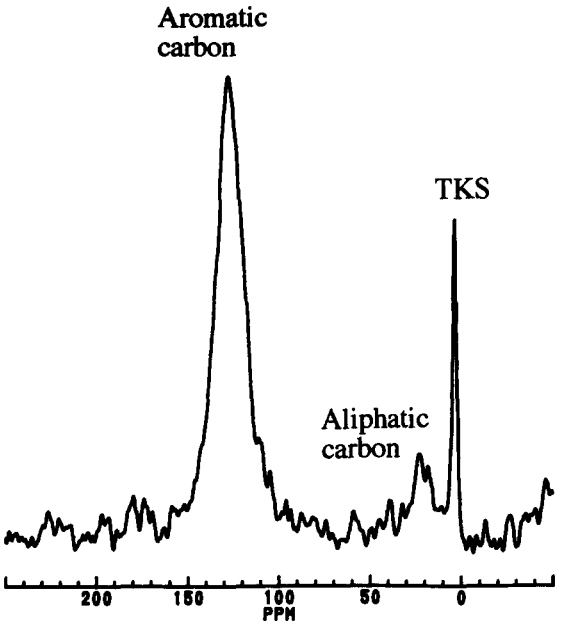

Fig. 6. SPE ^{13}C-NMR spectrum of the coke concentrate obtained from *n*-hexadecane after stripping the catalyst for 120 min.

3.6. *n-Hexadecane coke concentrates*

Fig. 5 compares the CP and SPE ^{13}C-NMR spectra of the coke concentrate obtained without stripping. This coke is a much more aliphatic character than for the refinery cokes analysed with the aromaticity (total sp^2 carbon) values derived from the CP and SPE spectra both being close to 0.82 (Table 1). However, the sp^2 carbon envelope in the spectra contains a small contribution from carboxyl and carbonyl groups (Fig. 5, approx. 2–3 mol% carbon, 175–205 ppm). This has probably arisen from accidental exposure of the coked catalyst to hot air during recovery from the fluidised-bed reactor. Assuming that aliphatic groups have oxidised preferentially, this means that the aromaticity may be somewhat lower (approx. 0.80) than that measured. The distribution of intensity in the aliphatic envelope in the ^{13}C-NMR spectra for this *n*-hexadecane coke is centred at approx. 30 ppm (Fig. 2), indicating that CH_2 dominates over CH_3.

The cokes obtained after stripping are highly aromatic with carbon aromaticities in excess of 0.90 (Fig. 6 and Table 1). The increase in aromaticity compared to the initial sample of approx. 10 mol% carbon (Table 1) compares with the overall carbon loss of approx. 15% obtained by stripping (from 1.5% to 1.3% (w/w)). This suggests that side-chain cracking is probably the primary mechanism responsible for the formation of volatiles during stripping. However, the information from the DD ^{13}C-NMR experiments on the initial and 120 min stripped coke reveal that there has also been a growth in aromatic ring size (Table 1). As for the refinery coke concentrates, the non-protonated aromatic carbon concentrations obtained from the DD experiments have been corrected for alkyl substituted carbons (estimated from the aliphatic carbon contents) to leave the proportion of aromatic carbon which is in bridgehead positions (Table 1). Although the proportions of non-protonated aromatic carbon are similar for the initial and stripped cokes, the latter contains more highly condensed aromatic structures as suggested by the mass spectrometry results. Bridgehead carbon accounts for 45% of the aromatic carbon in the stripped coke which, on average, corresponds to approximately 8–10 ring peri-condensed structures. However, such structures are considerably less condensed than those found in the refinery cokes where carbon in bridgehead positions accounted for over 50% of the aromatic carbon.

As well as the increase in the degree of condensation of the aromatic groups, the aliphatic region in the ^{13}C-NMR spectrum of the stripped coke indicates that CH_3 is the dominant aliphatic group (10–25 ppm) with no discernible peak at approx. 30 ppm from CH_2 (Table 1).

4. Conclusions

Fundamental deactivation studies on zeolites involving NMR thus far have generally involved extremely high concentrations of coke in relation to normal FCC operation to achieve sufficient sensitivity for characterising the catalytic coke by solid-state ^{13}C-NMR. Further, the results have generally been qualitative in nature due to the uncertainties over quantifaction with the CP technique. Nonetheless, for both FCC and hydroprocessing, the results have indicated how coke structure can vary as a function of catalyst type, feedstock and reaction severity.

To analyse catalytic coke at typical concentrations of approx. 1% (w/w) for refinery operations, it is essential to demineralise the aluminosilicate matrices

to concentrate the coke. As for other carbonaceous materials, the use of a relatively low-field field strength in conjunction with the single pulse excitation (SPE or Bloch decay) technique has enabled most of the carbon to be detected in FCC catalytic coke concentrates and, therefore, NMR-invisible graphitic layers are not thought to be major structural features of the samples investigated. Although stripping the catalysts gives rise to highly aromatic cokes, even for *n*-hexadecane, differences in feedstock composition are still reflected in the structure of the resultant cokes with those derived from *n*-hexadecane containing less condensed aromatic nuclei than those from heavy refinery feeds.

The application of solid-state ^{13}C-NMR to catalytic coke thus far has focussed primarily on hydroprocessing and FCC catalysts, but the methodology described here involving demineralisation is equally suitable for deactivated catalysts from other hydrocarbon conversion processes, such as dehyrogenation and reforming.

Acknowledgements

The authors thank the Engineering and Physical Sciences Research Council (EPSRC) for financial support of this work through grant no. GR/H/24990, including a studentship for B.J. McGhee.

References

[1] J.B. Butt, Adv. Chem. Ser., 109 (1972) 259 and refecences therein.
[2] R. Hughes, Deactivation of Catalysts, Academic Press, London, 1984.
[3] E.H. Wolf and A. Alfani, Catal. Rev. Sci. Eng., 24 (1982) 329 and references therein.
[4] D.L. Trimm, Appl. Catal., 5 (1983) 263 and references therein.
[5] R.M. Davidson, NMR studies of coal, IEA Review CR/08, 1988.
[6] M.A. Wilson, NMR Techniques and Applications in Geochemistry and Soil Chemistry, Pergamon Press, Oxford, 1987.
[7] C.E. Snape, Analysis of Fossil Fuels, in: L.D. Field, S. Sternhell (Eds.), Analytical NMR, Wiley, New York, NY, 1989, Ch. 4.
[8] C.E. Snape, D.E. Axelson, R.E. Botto, J.J. Delpuech, P. Tekely, B.C. Gerstein, M. Pruski, G.E. Maciel and M.A. Wilson, Fuel, 68 (1989) 547 and references therein.
[9] J.A. Franz, R. Garcia, J.C. Linehan, G.D. Love and C.E. Snape, Energ. Fuels, 6 (1992) 598.
[10] G.D. Love, R.V. Law and C.E. Snape, Energ. Fuels, 7 (1993) 639.
[11] M.M. Maroto-Valer, G.D. Love and C.E. Snape, Fuel, 73 (1994) 1926.
[12] W.A. Groten, B.W. Wojciechowski and B.K. Hunter, J. Catal., 125 (1990) 311.
[13] J.P. Lange, A. Gutsze, J. Allgeier and H.G. Karge, Appl. Catal., 45 (1988) 345.
[14] S.-B. Liu, S. Prasad, J.-F. Wu, L.-J. Ma, T.-C. Yang, J.-T. Chiou, J.-Y. Chang and T.-G. Tsai, J. Catal., 142 (1993) 664.
[15] N.O. Egiebor, M.R. Gray and N. Cyr, Appl. Catal., 55 (1989) 81.
[16] Y. Yoshimura, K. Hazamizu, T. Sato, H. Shimada and A. Nishijima, Fuel Process. Tech., 16 (1987) 55.
[17] P. Zeuthen, J. Bartholdy, P. Wiwel and B.H. Cooper, Stud. Surf. Sci. Catal., 88 (1994) 199.
[18] A. Foncesa, P. Zeuthen and J.B. Nagy, Fuel, 74 (1995) 1267.
[19] C.E. Snape, B.J. McGhee, J.M. Andresen, R. Hughes, C.L. Koon and G. Hutchings, Appl. Catal. A, 129 (1995) 125.
[20] B.J. McGhee, C.E. Snape, J. Andresen, R. Hughes, C.L. Koon and G. Hutchings, Prepr. Am. Chem. Soc. Div. Pet. Chem., 40 (1995) 379.
[21] A. Aziz, H. Mohammed, B.J. McGhee, J.M. Andresen, C.E. Snape and R. Hughes, Prepr. Am. Chem. Soc. Div. Pet. Chem., 41 (1996) 433.
[22] J.L. Bonardet, M.C. Barrage, J. Fraissard, M.A. Ferrero and W.C. Conner, Stud. Surf. Sci. Catal., 88 (1994) 265 and references therein.
[23] R. Hughes, G. Hutchings, C.L. Loon, B. McGhee and C.E. Snape, Stud. Surf. Sci. Catal., 88 (1994) 377.
[24] R. Hughes, G. Hutchings, C.L. Koon, B. McGhee, C.E. Snape and D. Yu, Prepr. Am. Chem. Soc. Div. Pet. Chem., 40 (1995) 413.