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A Nuclear Microprobe Examination of Catalysts Used in Hydrotreating and Hydroconversion of Petroleum Fractions

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Nuclear microprobe methods have been developed to measure light element and metallic poison distributions in used catalysts. The methods are based on the irradiation of sectioned catalyst pellets with microbeams of energetic (MeV) charged particles. Irradiation with deuterons allows the determination of carbon and nitrogen by nuclear reactions, and vanadium, nickel, and other elements with atomic number >12 by particle-induced X-ray emissions. Hydrogen can be determined by an elastic recoil analysis method based on irradiation with helium ions. The development of the methods for catalyst applications is described. All elements can be determined at concentrations of <0.1 wt% at spatial resolutions as high as 5 μm. The methods have been applied to examine hydrotreating and hydroconversion catalysts used to treat heavy petroleum fractions. The extent of intra- and interpellet variations in deposited elements has been found to be high, but statistically acceptable average distributions can be obtained by examining no less than five pellets per batch. The interrelationship between deposited elements has been examined. An observation is that the H/C atom ratio of coke falls in regions of pellets containing high concentrations of vanadium. Early work indicates that nitrogen compounds tend to form coke nearer the surface of pellets than hydrocarbons. Information has been obtained on pore filling. © 1995 Academic Press, Inc.

1. INTRODUCTION

The deactivation of catalysts used in the hydrotreating and hydroconversion of heavy petroleum feedstocks is associated with coking and the deposition of metallic poisons (1–4). The influence of coking on catalyst deactivation is not well understood. Coking and metallic fouling have been the subjects of recent studies through two collaborative programmes supported by the EEC Commission (5, 6). Overall, these programmes have involved several catalysts, principally of the NiMo and CoMo types, and a number of feedstocks including pure model compounds and heavy petroleum fractions treated using pilot test units under industrial conditions. The application of nuclear microprobe analysis for the examination of used hydrotreating and hydroconversion catalysts is novel and is described in detail.

Nuclear microprobe methods of analysis use focused microbeams of energetic (MeV) charged particles, for instance protons or helium ions, to measure the distribution of elements and isotopes in materials (7, 8). Light elements may be determined by nuclear reaction analysis (NRA) and elastic recoil analysis (ERA), whereas medium and heavy elements can be measured more readily by particle induced X-ray emission (PIXE) or by Rutherford backscattering (RBS). The energetic charged particles are often produced by a Van de Graaff accelerator and focused by quadruple magnets to micrometer-size beams. These are scanned across samples held in a target chamber; the radiations emitted by the interaction of the beam and sample are detected, and compared with those from standards to determine variations in the sample composition with position. The Harwell nuclear microprobe is described in detail elsewhere (9, 10) as are typical applications of the equipment (7, 8).

Prior to the current programmes, nuclear microprobe analysis had been used to a limited degree for the examination of coked catalysts (11, 12). A method of measuring carbon distributions, based on the reaction $^{12}C(d, p)^{13}C$, was described in a Short Communication (11). A preliminary study of the determination of hydrogen distributions was based on forward recoil of protons by ^{3}He ions (12). These methods have been further developed for the measurement of carbon and hydrogen distributions, respectively. Deuteron ($^{2}H^{+}$ion) irradiation has also been employed to measure nitrogen distributions using the reaction $^{14}N(d, p)^{15}N$. Simultaneous measurement of the distribution of metallic deposits, e.g., V and Ni, and of the catalyst components has been found to be possible using PIXE. A number of aspects of method development are described, notably equipment, catalyst pellet preparation and, most importantly, sample decomposition during analysis.

This investigation had a number of aims which ranged

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from study of the variability of profiles in pellets from a sample batch, through investigation of relationships between coke components and deposited metals, to kinetic aspects of catalyst performance and its degradation. These topics and aspects of method development are described and discussed.

2. METHODS

2.1. *The Basis of the Nuclear Microprobe Methods*

At the outset of the programme, the intention was to develop methods for the measurement of the distribution of carbon, hydrogen, nitrogen, and deposited metals in used hydroprocessing catalysts.

The measurement of light elements should be achieveable by nuclear reaction analysis and elastic recoil analysis. Interactions of the following types were consequently investigated for the determination of carbon, nitrogen and hydrogen:

$$\left.\begin{array}{l} {}^{12}\mathrm{C(d,\ p)}{}^{13}\mathrm{C} \\ {}^{14}\mathrm{N(d,\ p)}{}^{15}\mathrm{N} \\ {}^{12}\mathrm{C}({}^{3}\mathrm{He,\ p}){}^{14}\mathrm{N} \\ {}^{14}\mathrm{N}({}^{3}\mathrm{He,\ p}){}^{16}\mathrm{O} \end{array}\right\}\text{Nuclear Reactions}$$

$$\left.\begin{array}{l} {}^{1}\mathrm{H}({}^{3}\mathrm{He},\ {}^{3}\mathrm{He}){}^{1}\mathrm{H} \\ {}^{1}\mathrm{H}({}^{4}\mathrm{He},\ {}^{4}\mathrm{He}){}^{1}\mathrm{H} \end{array}\right\}\text{Elastic Recoil}$$

These methods had predictable sensitivities of <0.1 wt% and were potentially suitable for the planned work. In addition, metallic poisons such as vanadium, iron, and nickel should be measurable simultaneously by particle induced X-ray emissions, with similar sensitivities:

$$\left.\begin{array}{l} \mathrm{M}(d,\ d\ \text{X-ray})\mathrm{M} \\ \mathrm{M}({}^{3}\mathrm{He},\ {}^{3}\mathrm{He}\ \text{X-ray})\mathrm{M} \\ \mathrm{M}({}^{4}\mathrm{He},\ {}^{4}\mathrm{He}\ \text{X-ray})\mathrm{M} \end{array}\right\}\text{Particle induced X-ray emission}$$

Rutherford backscattering was also employed to investigate sample composition but to a very limited degree.

In principle, methods employing ${}^{3}\mathrm{He}^{+}$ ion irradiation were the most attractive, offering the potential of simultaneous determination of carbon, hydrogen, nitrogen and metallic poisons, and they were investigated. However, in practice, methods based on ${}^{2}\mathrm{H}^{+}$ and ${}^{4}\mathrm{He}^{+}$ irradiation proved to be more readily applicable.

During method development, equipment and sample preparation methods were optimized, and the ion irradiation techniques were studied to establish the extent of interferences, the influence of ion beam damage and the quantification of results.

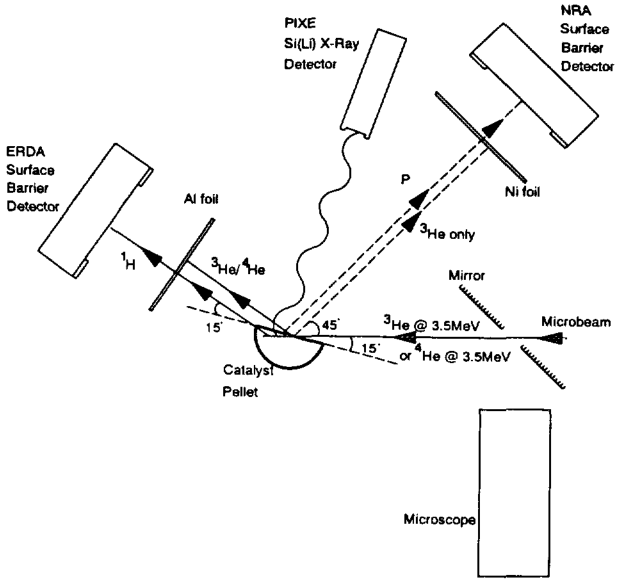

FIG. 1. Detector and target arrangement for the analysis of catalysts by elastic recoil detection analysis, nuclear reaction analysis, and particle induced X-ray emission.

2.2. *Equipment Development*

The determination of the hydrogen content of samples by elastic recoil analysis demands the use of special irradiation geometries to allow the observation of protons recoiled from thick samples in a forward direction. The type of arrangement used for both ${}^{3}\mathrm{He}^{+}$ and ${}^{4}\mathrm{He}^{+}$ irradiation is shown in Fig. 1. The incident ion beam is inclined to the sample surface at an angle of 15° and recoiled protons are detected at an identical angle in the forward direction. Interference from scattered helium ions is prevented by their absorption in an aluminium foil placed in front of the detector. The sample holder must be constructed with care to avoid any mechanical obstruction of the ion beam and recoiled protons. A Si(Li) detector observes X-rays produced by particle irradiation. A silicon surface barrier detected is also shown, and this was used to detect particles emitted by nuclear reactions induced during ${}^{3}\mathrm{He}^{+}$ ion irradiation.

To avoid carbon or hydrogen build-up on sample surfaces, the target chamber pressure must be maintained below 10^{-6} mbar. Without this precaution, which involves the use of a large cryogenic trap close to the sample, the ion beam cracks residual hydrocarbons in the target chamber vacuum, which leads to surface deposition on the target and interference in the determination of carbon and hydrogen.

2.3. *Catalyst Experiments*

(a) Catalysts. A commercial NiMo catalyst (Haldor Topsøe TK 771, 1/32 in. cylindrical) containing 3.4%

NiO, 14.3% MoO_3, and 2% P and a commercial CoMo catalyst (Haldor Topsøe TK 770, 1/16 in. cylindrical) containing 3.5% CoO and 14.4% MoO_3 both supported on the same alumina carrier were the principal catalysts used in this study.

(b) Catalyst performance tests. In order to study the interplay between coke and metal deposition during typical test runs by the described method, spent samples were collected from experiments using an oil fraction, atmospheric residue, from Kuwait as feedstock. The tests were performed in constant HDS mode, where the reactor temperature was increased from approximately 365°C at start of run (S.O.R). to maintain 90% HDS to about 405°C at end of run (E.O.R). in order to compensate for deactivation. The length of the experiments varied for the different tests. Apart from the differences in reactor temperature, all other process parameters for the experiments were nearly the same. Tests with NiMo catalysts were performed at LHSV = 0.28 h^{-1} and P = 123 atm, and the test with CoMo catalyst was performed at LHSV = 0.35 h^{-1} and P = 130 atm.

The catalysts were presulfided for 24 h at 350°C and 100 atm using a straight-run heavy Arabian vacuum gas oil (VGO). After completion of the presulfiding and introduction of the test conditions, the feedstock was introduced.

The catalyst performance tests were carried out in bench-scale isothermal trickle-bed reactors. The reactor was loaded with 80 cm^3 catalyst extrudates in a composite catalyst bed. The third catalyst in the bed was either TK 771 or TK 770. The catalyst was diluted with 0.2–0.3-mm diameter (50–80 mesh) inert glass beads in order to improve the liquid distribution and contacting efficiency within the reactor.

The used catalysts were soxhlet extracted in xylene followed by drying at 200°C.

Sample NT 170 and NT 146 were NiMo catalysts which had been exposed to the feed for 2500 and 7500 h, respectively. Sample CT 601 was the CoMo catalyst exposed for 4100 h. These catalyst samples were typically split into three fractions. The top fraction was marked "top," the middle "mid," and the bottom "bot".

2.4. *Sample Preparation*

To determine hydrogen by elastic recoil analysis, sectioned samples must be prepared with flat well-polished surfaces to avoid errors from surface topography. A surface free from contamination is also essential and the retention of polishing powders or their suspending liquids must be avoided.

The polishing technique ultimately perfected involved the use of fine zirconia polishing powder suspended in xylene. The powder had a hardness suitable for polishing the alumina-based catalyst pellets, whilst xylene was ideal as all the catalysts had been extracted with boiling xylene after use to remove residual feed and to leave coke. Ultrasonic cleaning effectively removed residual zirconia. Vacuum drying at 50°C removed residual xylene leaving polished surfaces suitable for subsequent nuclear microprobe examination.

2.5. *Investigation of Methods*

To aid the investigation of methods of analysis for the determination of the distribution of light elements and metallic poisons in used catalysts, standards were prepared or procured. Coked catalyst standards were prepared from ground pure oxides and standard petroleum coke as compressed pellets with smooth surfaces. Hydrogen standards in pure zirconium metal were prepared by high temperature equilibration. Standards containing 10,000 and 1,000 ppm of hydrogen by weight were used and were stable under ion beam irradiation. Steel standards containing known amounts of nitrogen and carbon were employed, again because of their radiation stability. All metallic standards were sectioned, mounted, and polished prior to use.

The determination of carbon, nitrogen, and metals using irradiation with 1.3 MeV deuteron ($^2H^+$) microbeams proved to be relatively simple. The sensitivities attainable for carbon and metals were entirely adequate, allowing their measurement well below the predicted sensitivities, 0.1 wt% Whilst a sensitivity of less than 0.1% (wt) could be attained for the determination of nitrogen, this concentration is much closer to the detection limit, and results at and below this concentration are subject to large statistical errors. The principal problem encountered was the decomposition of some samples during analysis as a result of ion beam damage. This type of damage lowered the carbon concentration with an increase in the irradiation dose. The problem could be minimized by lowering beam current densities. This could be achieved most effectively by scanning the beam continuously across the sample, at kHz rates, and damage was reduced to an imperceptible level for most samples. Consequently, during the analysis of coked catalysts, the standard practice adopted was to scan the beam continuously across the sample, keeping beam current densities down to ca. 0.07 pA μm^{-2}. This was achieved by spreading a 5-nA beam over an area of 1500 × 50 μm across the diameter of a sectioned and polished catalyst pellet. The rate of accumulation of protons emitted by the reaction $^{12}C(d, p)^{13}C$ was observed with deposited charge (μC), and any losses of carbon caused by beam damage could be detected and corrected for by linear extrapolation of the results to zero charge, as shown in Fig. 2.

$^3He^+$ ion irradiation is potentially suitable for the simultaneous determination of hydrogen, carbon, nitrogen

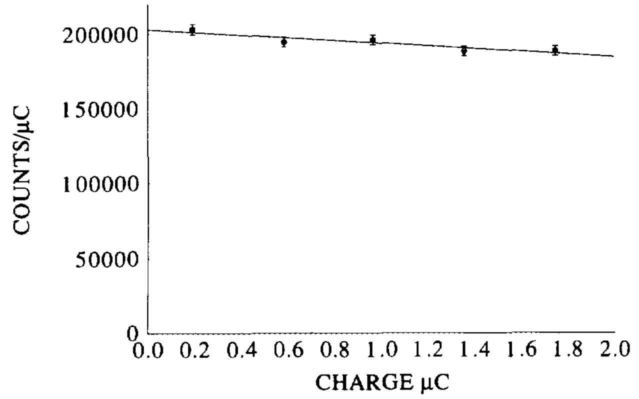

FIG. 2. Losses of carbon from used TK 771 catalyst pellet (run NT 146-top) during irradiation with 1.3 MeV deuterons. Counts per unit charge against cumulative charge.

and metallic poisons in coked catalysts; however, some problems have been encountered during its use. To obtain good yields of emitted particles from the nuclear reactions $^{12}C(^{3}He, p)^{14}N$ and $^{14}N(^{3}He, p)^{16}O$, it is necessary to use relatively high energy, 3.5 MeV $^{3}He^{+}$ ions. However, protons emitted by these reactions, and the reaction $^{16}O(^{3}He, p)^{18}F$, were detected simultaneously with elastically recoiled protons from hydrogen in the sample. The energy spectra of the recoiled protons and the protons emitted by the reactions overlapped significantly. The yield of recoiled protons was between one and two orders of magnitude higher than that from the reactions on carbon and oxygen.

To avoid the interferences encountered when measuring hydrogen by $^{3}He^{+}$ ion irradiation, $^{4}He^{+}$ ion irradiation was adopted instead because reactions with light elements are much less readily induced by this alternative bombarding particle, and correction for interference by carbon and oxygen is not needed. However, adopting this procedure necessitates the use of two successive irradiations of the same sectioned catalyst pellet across the same diameter, particularly to produced readily relatable information on the distributions of hydrogen and carbon, and to allow the derivation of meaningful H/C atom ratios. In practice, deuteron irradiation is employed initially to measure carbon, nitrogen and metal distributions. The sample surface is lightly repolished to remove any beam damaged material. Then the hydrogen is determined by irradiation of the sample across the same diameter with a beam of 3.5 MeV $^{4}He^{+}$ ions. For all samples examined, beam damage of the coke caused hydrogen losses during analysis. Consequently, the continuous scanning procedure was again employed with observation of the rate of fall of the recoiled proton yield with deposited charge. Following the observation of Kirby and Legge (13) that irradiation of biological specimens with 2-MeV $^{4}He^{+}$ ions caused hydrogen losses that could be described by the sum of two exponential functions, the loss curves observed for coked catalysts were fitted to the same type of function. Typical curves for two catalyst samples are shown in Fig. 3 together with the curve for the 10,000 ppm (wt) hydrogen in zirconium standard. The first two curves, (a) and (b), compare amples of an uncoked catalyst with a coked catalyst. The result for the pellet of unused TK 771 shows that the hydrogen content is lower than that of the used pellet of TK 770 from run CT601. The hydrogen in the former is probably present as water bound to the alumina both weakly and strongly. The hydrogen in the latter is not only more abundant but also, in part, covalently bonded to carbon. This specimen contains relatively light coke with a high H/C atom ratio, which is reflected by the similar size of the fast and slow loss components. For heavier cokes, the slow loss component predominates, reflecting their near graphitic structure.

The curve for the hydrogen in zirconium standard shows no evidence of hydrogen loss under irradiation, confirming the stability of this standard. The recoiled proton yield at zero deposited charge can be readily derived for coked catalyst samples from the fitted curve. Whilst this method proved effective and shed some light on the composition of the coke, it depended on observing hydrogen losses during the deposition of at least 1 μC of the charge. Reassessment of the data indicated that fitting simple functions to the early observation points was equally effective in determining the recoiled proton yield at zero charge. Subsequently, a single exponential function was fitted to data collected during the deposition of the first 0.3 μC of charge.

Quantification of the hydrogen results depends not only on being able to assess the yield of recoiled protons at zero deposition of charge but also on the fitting of a simulated proton recoil yield curve to the observed proton recoil spectra of standards and samples. The agreement between the simulated and observed proton recoil spectra is good when using a proton recoil cross section mentioned in a recent publication by Tirira and co-workers (14). Typical simulated and observed spectra are shown in Fig. 4 for a hydrogen in zirconium standard and a coked catalayst pellet. For the latter it is clear that there are virtually no protons with energies above the recoil region, confirming that $^{4}He^{+}$ ion irradiation induces few if any nuclear reactions in carbon and oxygen. Fitting a simulated curve to the observed curve for the standard allows experimental parameters, notably the solid angle interrogated by the detector, to be determined for subsequent application in the simulation of sample spectra. The simulation of a sample spectrum automatically produced a hydrogen concentration by a process that compensates for the catalyst composition and its secondary

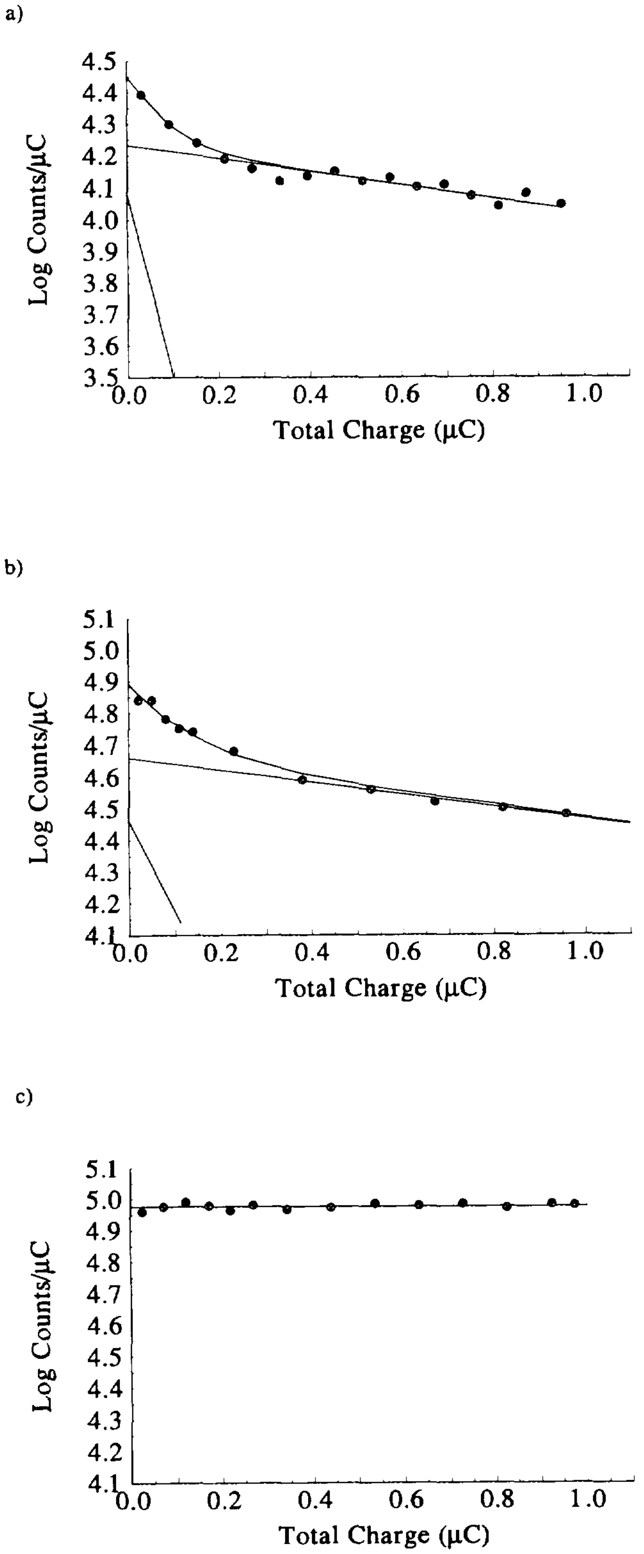

FIG. 3. Loss of hydrogen from: (a) unused TK 771; and (b) used TK 770 from the CT 601 run, 4100 h exposure; (c) hydrogen standard 10,000 ppm (wt) in zirconium. Irradiated with 3.5 MeV $^4He^-$; log proton counts per unit charge against cumulative charge fitted to two exponential functions, shown as straight lines.

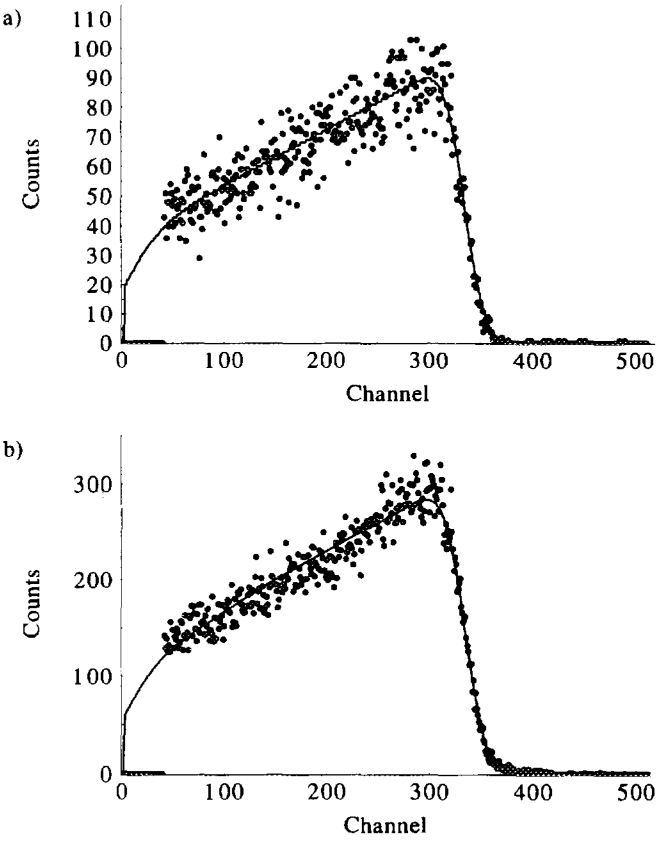

FIG. 4. Observed and fitted proton recoil spectra; irradiation with 3.5 MeV $^4He^+$ ions; (a) used TK 771 pellet (run NT 146-mid); (b) hydrogen standard 10,000 ppm (wt) in zirconium.

influence on the recoiled proton yield per percent of hydrogen.

The validity of the nuclear microprobe methods for the determination of carbon, hydrogen, nitrogen, and metallic foulants can be demonstrated by comparison of the nuclear microprobe results with bulk chemical analyses, as noted later.

3. RESULTS AND DISCUSSION

Nuclear microprobe methods of analysis have been applied to measure the distributions of carbon, hydrogen, nitrogen, metallic poisons, and support components in a considerable number of coked catalysts used in the hydrotreating and hydroconversion of petroleum fractions. Examples have been selected to illustrate the value of the observations in achieving a number of objectives. These included:

(*1*) *establishing the variability of deposited element* distributions within batches of used catalyst both on an inter- and intrapellet basis;

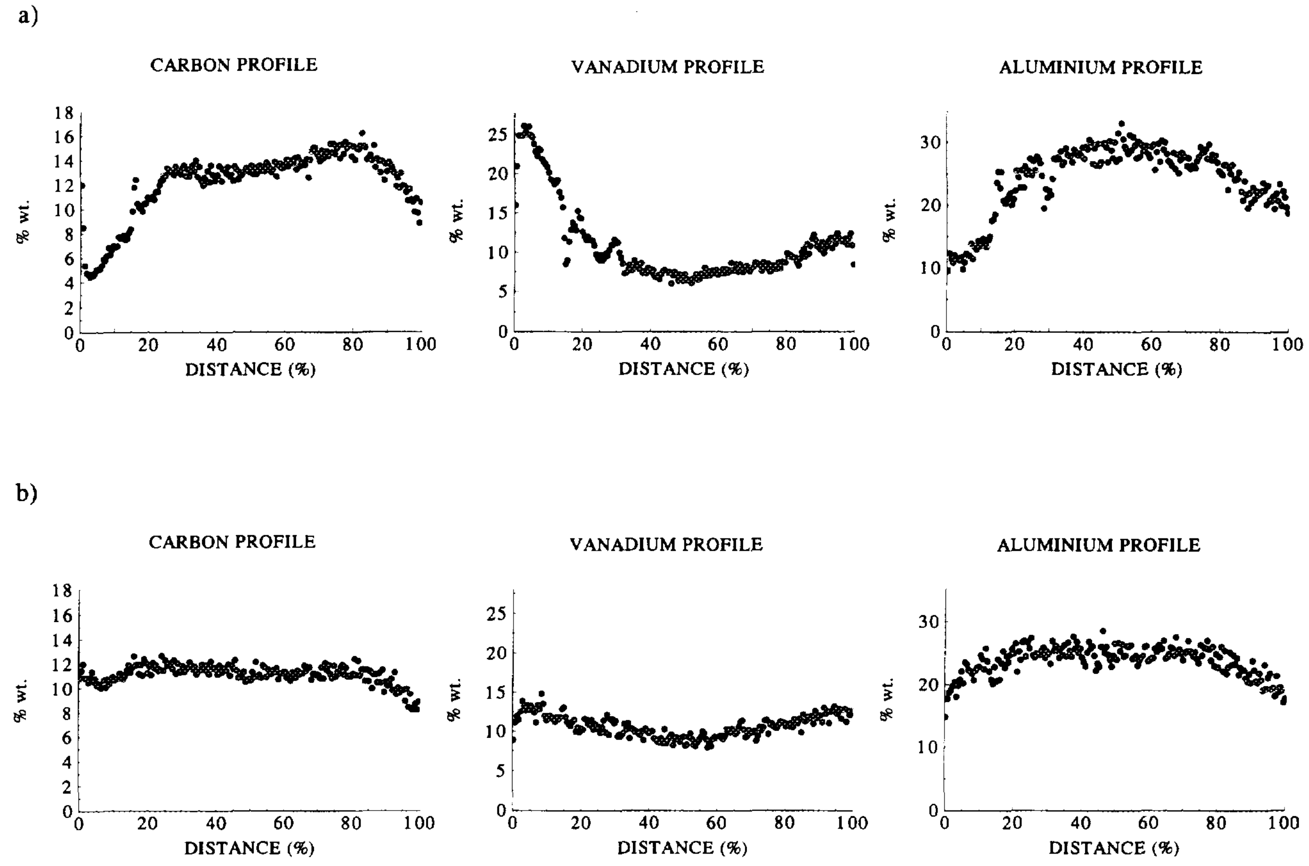

FIG. 5. Variations in the distributions of carbon, vanadium, and aluminium, weight percent against percentage distance across pellet diameter, in sections of two used TK 771 catalyst pellets from run NT 170-top (a) pellet B, (b) pellet D.

(2) seeking relationships between the build-up of deposits in catalysts during use;

(3) studying the influence of processing conditions and feedstocks on the performance and coking of catalysts;

(4) seeking kinetic effects that influence the deposition of coke and metallic poisons in catalysts during their use.

Progress towards the achievement of these objectives is described.

3.1. Variations in the Distribution of Coke in Batches of Used Catalyst

A considerable body of information has been gathered that emphatically demonstrates extensive variability in the distribution of coke and other deposits in batches of used catalyst both on an inter- and intrapellet basis.

Intrapellet variations have been observed either by detecting asymmetry in the distribution of components across a pellet diameter or by finding differences between the distributions measured for perpendicular diameters across a sectioned pellet. An example of the former is shown in Fig. 5. These relatively high spatial resolution scans across two pellets from sample NT170-top show that the distributions of carbon and vanadium were markedly asymmetric in pellet B but only marginally so in pellet D. The results also demonstrate intrapellet variation.

Interpellet variations can be observed by measuring the distributions of coke and metallic poisons across a representative number of sectioned pellets. A measure of the spread in results may be obtained by calculating the standard deviations of the averaged distributions along a pellet radius. The observations are logically related to a radius rather than a diameter, because the latter is not comparable between pellets, as their relative angular dispositions are indeterminate. For convenience, the radial distribution is usually presented as a symmetrical pseudodiametral distribution.

Further observations, at a lower spatial resolution, of the distributions of carbon and vanadium in 10 pellets from sample NT170-top emphasized the wide spread in the distributions of these elements. However, the average behaviour of the material can be obtained and is represented by the average distributions shown in Fig. 6. The error bars indicated the standard deviations (1σ) of

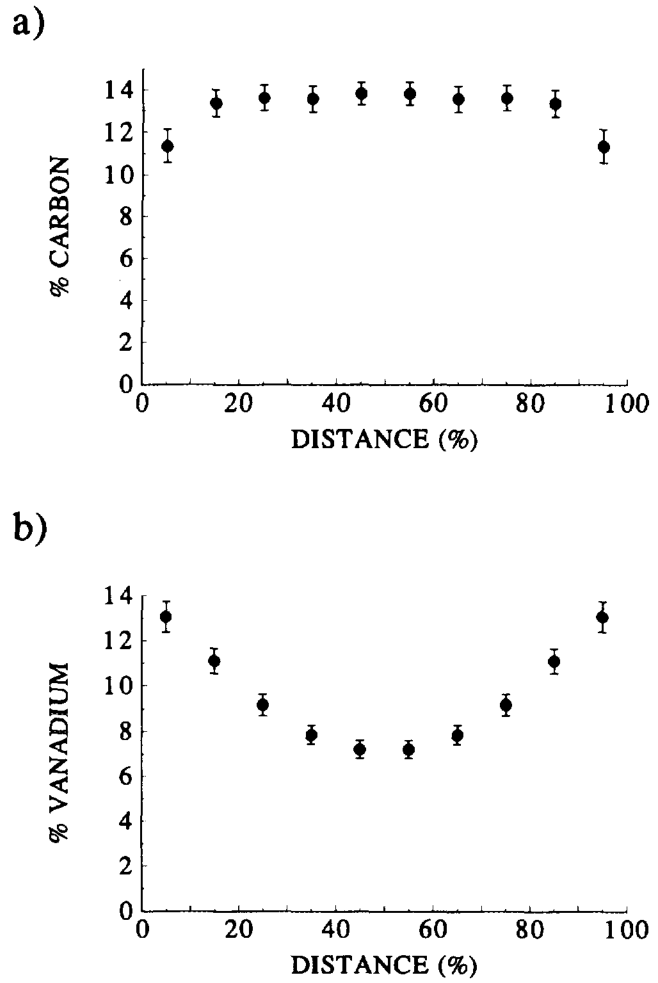

FIG. 6. Average elemental distributions for 10 used TK 771 catalyst pellets exposed in a trickle bed reactor, with error bars, $\pm 1\sigma$; (a) carbon (wt%); (b) vanadium (wt%), against percentage distance across pellet diameter.

the elemental concentrations at each analysis position and are rather less than 10% on a relative basis.

For sample NT170-top, the catalyst was exposed to the feed (on stream) in a trickle bed reactor. The asymmetric coke distribution was probably caused by uneven flow on the feed through the reactor bed rather than differences in pellet structure. Variations in the pellet environment might be less in large reactors as well as in ebullating bed reactors as compared with these examples.

Kinetic information on the deposition of coke and metallic poisons in catalysts must be acquired with considerable caution. To observe the average behaviour of catalyst pellets from a reactor or a region of a reactor, a statistically significant number of observations must be made. Experience indicates that acquisition of acceptable distribution data requires the examination of not less than five pellets per sample batch.

3.2. Relationships Between Coking and the Deposition of Metallic Poisons in Catalyst Pellets

Several studies have been made of the interdependence of the deposition of elements on catalysts during their use for hydrotreating and hydroconversion of petroleum fractions. Results from one, based on the use of the NiMo catalyst (Haldor Topsøe TK 771) sample NT 146, to treat an atmospheric residue feed in a trickle bed reactor, for ca 7500 h is used to illustrate the type of information that can be obtained. For this study a relatively large number of pellets of each sample type (six) were taken for nuclear microprobe analysis. Each sectioned, mounted, and polished pellet was subjected to irradiation with deuterons to measure its carbon, nitrogen and vanadium distributions. Pellets with well-defined carbon distributions, close to the average, were then selected for hydrogen measurement, normally two per sample batch. This procedure was adopted to minimize analysis effort.

The TK 771 catalyst used to treat an atmospheric residue in a trickle bed reactor for 7500 h was split into three fractions. Material from the top of the bed was designated NT146-top, that from its middle NT146-mid, and that from its bottom NT146-bot. All three materials were examined by means of the Harwell nuclear microprobe. The results are summarized in Figs. 7A, 7B, 7C, and 7D. Mean distributions for hydrogen, carbon, nitrogen, and vanadium are presented, expressed as volume percentages, with their associated errors or spread. The volume percentages were derived from the weight percentages by normalization against the support component aluminium. Without normalization, the near surface concentrations of many components appear to fall because of the diluting influence of the material deposited in catalyst pellet porosity. The elemental distributions expressed in volume percentages indicate their build-up from pellet surfaces into their interiors.

Before discussing the interrelationships between the distributions of the elements in pellets from sample NT146-top, -mid, and -bot, the mean elemental results derived from the nuclear microprobe analyses are compared with the values obtained by bulk chemical analyses (see Table 1). Overall, the results are in reasonable agreement considering the possible sampling error. The nuclear microprobe results for carbon, nitrogen, and hydrogen are consistently higher than those obtained by bulk analyses, perhaps suggesting some degree of bias between the methods. On the contrary, the vanadium results obtained by nuclear microprobe analysis tend to be lower than the bulk analysis results. Even so, the trends in composition revealed by the two sets of results are the same. Consequently, reasonable confidence can be placed in the conclusions drawn from the nuclear microprobe results.

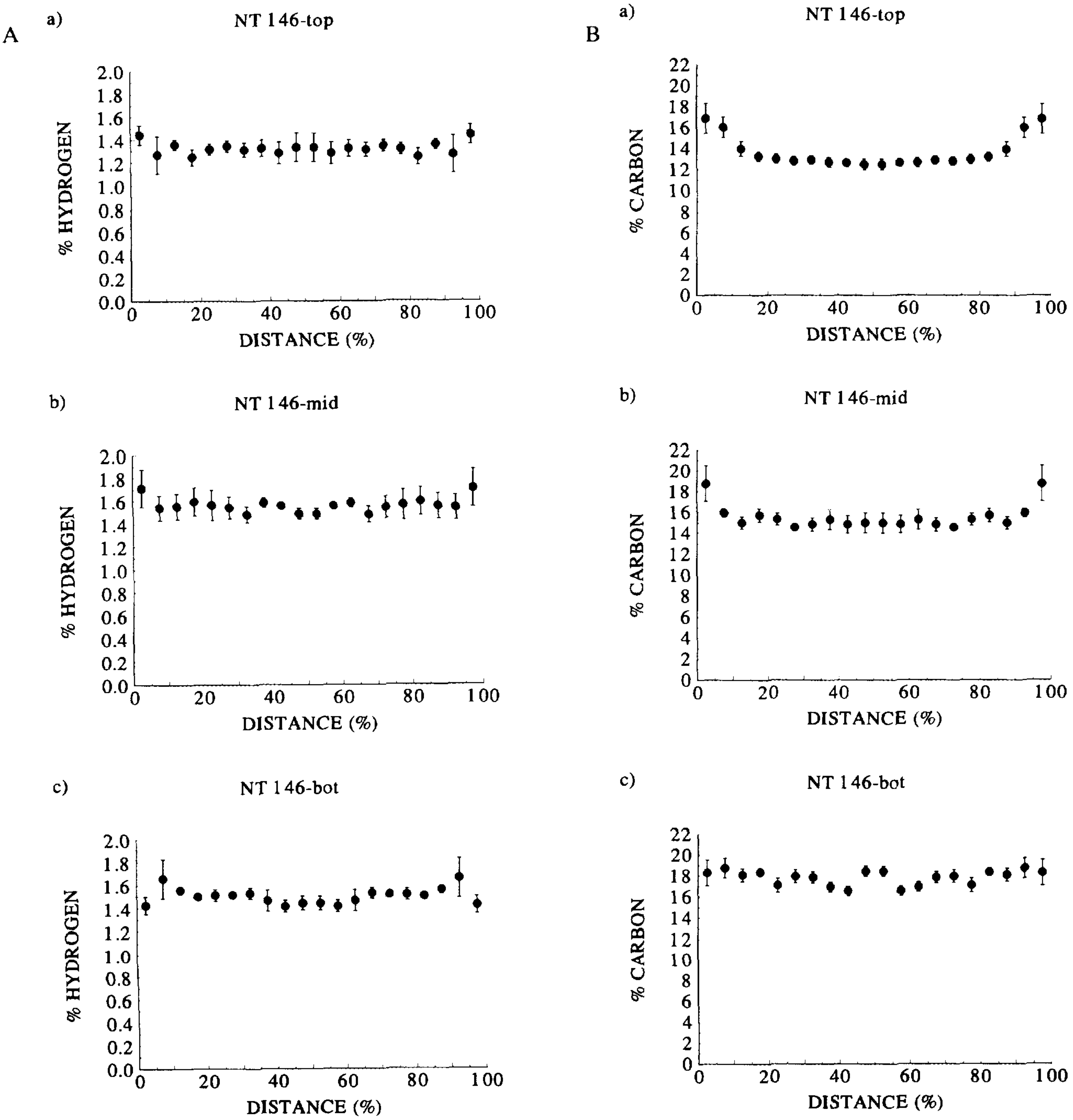

FIG. 7. Average elemental distributions, normalized to aluminium, for the TK 771 catalyst exposed in (a) the top (NT 146-top), (b) middle (NT 146-mid) and (c) bottom (NT 146-bot) of a trickle bed reactor. Error bars $\pm/1\sigma$. A hydrogen (vol %), B carbon (vol%), C nitrogen (vol%) and D vanadium (vol%).

The deposition of carbon in catalyst pellets tends to increase down the bed, which is not unexpected. This is accompanied by a flattening of its distribution within pellets. The concentration of hydrogen tends to increase marginally down the reactor bed, whereas its within-pellet distribution is virtually flat. However, no significant change in the nitrogen concentration occurs down the reactor bed: the catalyst pellets all contain more nitrogen at their peripheries than at their centres. Vanadium deposition decreases down the reactor, as might be expected, and its distribution within pellets is sharply surface peaked. An inverse relationship between the concentra-

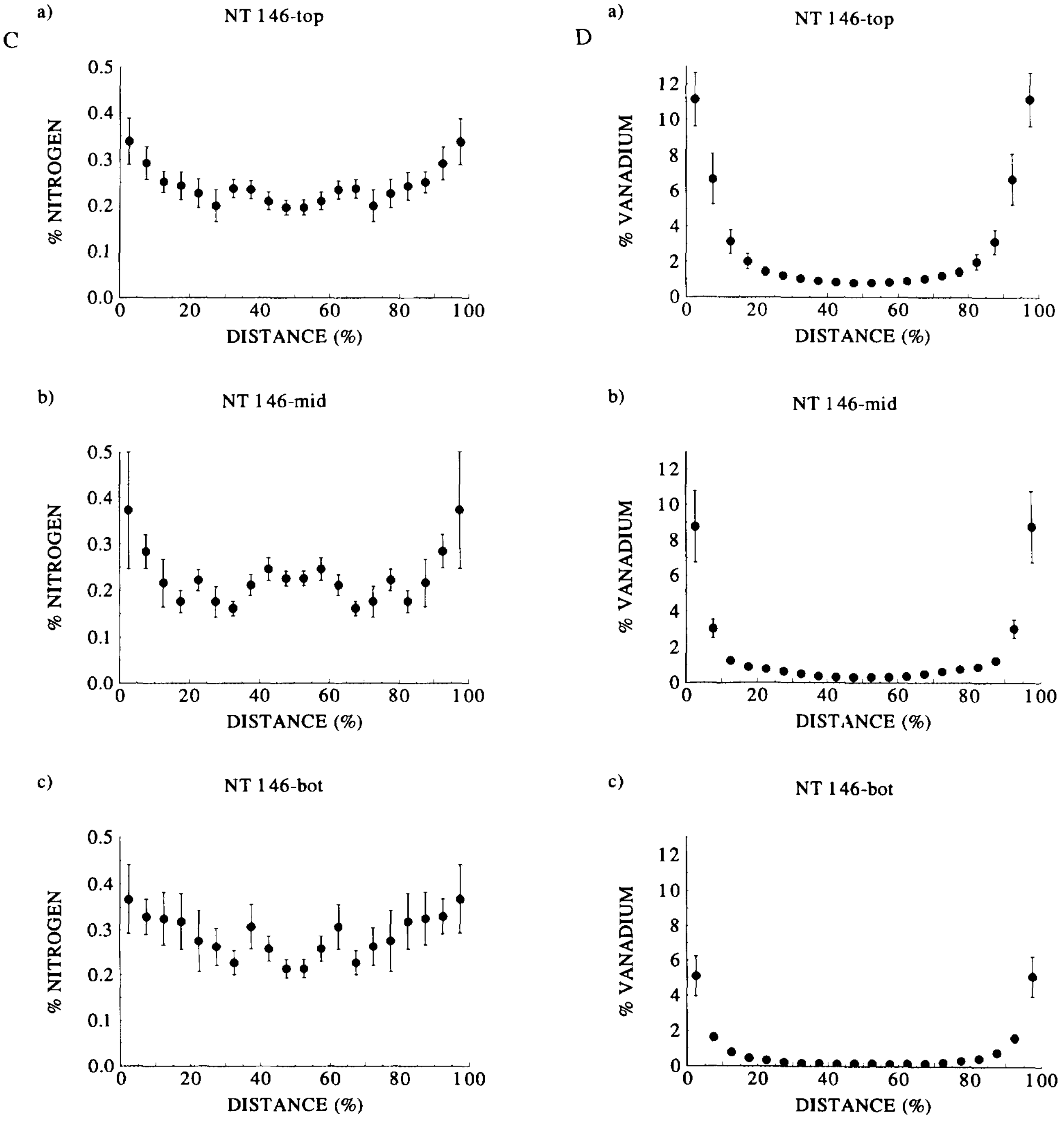

FIG. 7—*Continued*

tions of carbon (coke) and vanadium in catalysts down reactor beds is often observed. The similarities of the profiles of the various elements across the catalyst pellets show, however, that there is no direct, inverse relationship between vanadium and carbon. Overall, the results tend to indicate that movement of the four elements into catalyst pellets is in the order hydrogen, carbon, nitrogen, and vanadium. This may be due to the inherent mobility of molecules containing these elements or because of their propensity to deposit in catalyst pellets.

The rapid removal of vanadium both at the reactor top and near pellet peripheries is probably attributable to the high propensity of porphyrin molecules to deposit in catalyst pores.

The steadily increasing level of coke down the catalyst bed suggests that coke deposition is caused by a consecu-

TABLE 1

Comparison of Carbon, Vanadium, Nitrogen, and Hydrogen Results for Samples from Runs NT146-top, -mid, and -bottom, Obtained by Nuclear Microprobe Analysis and Bulk Analysis

		Concentration of element (%)							
		Carbon		Vanadium		Nitrogen		Hydrogen	
Material	Wt% or Vol% based result	Probe	Bulk[a]	Probe	Bulk[a]	Probe	Bulk[a]	Probe	Bulk[a]
NT146-top	Wt%	10.75	8.72	3.02	—	0.19	0.14	1.00	0.92
	Vol%[b]	14.37	13.5	4.38	5.3	0.29	—	1.34	—
NT146-mid	Wt%	11.05	10.15	1.51	—	0.16	0.17	1.13	0.90
	Vol%[b]	15.95	14.3	2.66	3.0	0.24	—	1.58	—
NT146-bot	Wt%	13.74	12.03	0.89	—	0.22	0.20	1.14	0.90
	Vol%[b]	18.03	16.4	1.48	1.9	0.31	—	1.52	—

[a] Bulk chemical analysis.

[b] Probe results normalized to aluminium, bulk results normalized to molybdenum.

tive reaction, as suggested by Froment and Bischoff (15) and recently discussed by Bartholdy and Cooper (16). This, however, is inconsistent with the shape of the carbon profiles in the catalyst pellets. Polyaromatic hydrocarbons may deposit near the top of the reactor bed and close to pellet peripheries, because of their high degree of absorption by catalysts (17). This could explain the high near-surface carbon concentration in pellets from sample NT146-top, coking at their centres being impeded physically by the high carbon and vanadium concentrations at pellet surfaces. Lower down the reactor bed, smaller more mobile coke precursors will more readily penetrate to pellet centres, ultimately producing high coke concentrations throughout.

Whilst the results for nitrogen are subject to relatively large errors, these and other results suggest that compounds which deposit nitrogen penetrate catalyst pellets less readily than hydrocarbons, because nitrogen concentrations fall gradually from the surface of pellets to their centres. From discussion in the recent literature concerning nitrogen distribution it has been concluded that nitrogen is present as inorganic as well as organic nitrogen species adsorbed on the catalyst (18). It is further suggested by Zeuthen *et al.* (18) that nitrogen is not intimately associated with the coke, but rather that the adsorbed nitrogen is covered by a coke layer without nitrogen. This supports these results showing that there is no correlation between N and C distributions in the catalyst pellets.

In seeking interrelationships between the distributions of elements within these catalyst pellets, the H/C atom ratios were derived from material from the top, middle and bottom of the reactor. The way in which this ratio varies is shown in Fig. 8. This is simply the atom ratio based directly on the nuclear microprobe results. The H/C ratio is, however, higher than what is believed to be representative of the coke, since it is known that the uncoked catalyst contains approx. 0.6 wt% of hydrogen on average, commonly associated with the catalyst support and metals. For the top sample with high vanadium concentration, the ratio falls towards the pellet surface. This relationship has also been observed for coke in other used catalysts which have high near-surface concentrations of vanadium. These observations possibly suggest that coke produced in the presence of vanadium is more graphitized because it can be less readily hydrogenated. Whilst less coke tends to be found in catalysts which contain high vanadium concentrations, the mechanism predominately involved is probably physical exclusion of coke precursors because of the presence of deposited vanadium rather than the reduced ability of the catalyst to hydrogenate the coke.

Although results for this atmospheric residue run clearly demonstrate differences in the H/C atom ratio across coked catalyst pellets, which strongly correlate with the deposition of vanadium, observation of the N/C atom ratio was much less informative. As noted above, these and other nitrogen results suggest that the movement of nitrogen into catalysts is less rapid than carbon. Whilst this could be associated with strong interaction of heterocyclic nitrogen compounds such as carbazoles with the catalyst support, nitrogen deposition during catalyst coking merits further investigation.

3.3. *The Study of Pore Filling*

The presence of large concentrations of elements such as carbon and vanadium in used catalyst pellets implies that much of the porosity has been filled. The degree of pore filling can be calculated from the composition of

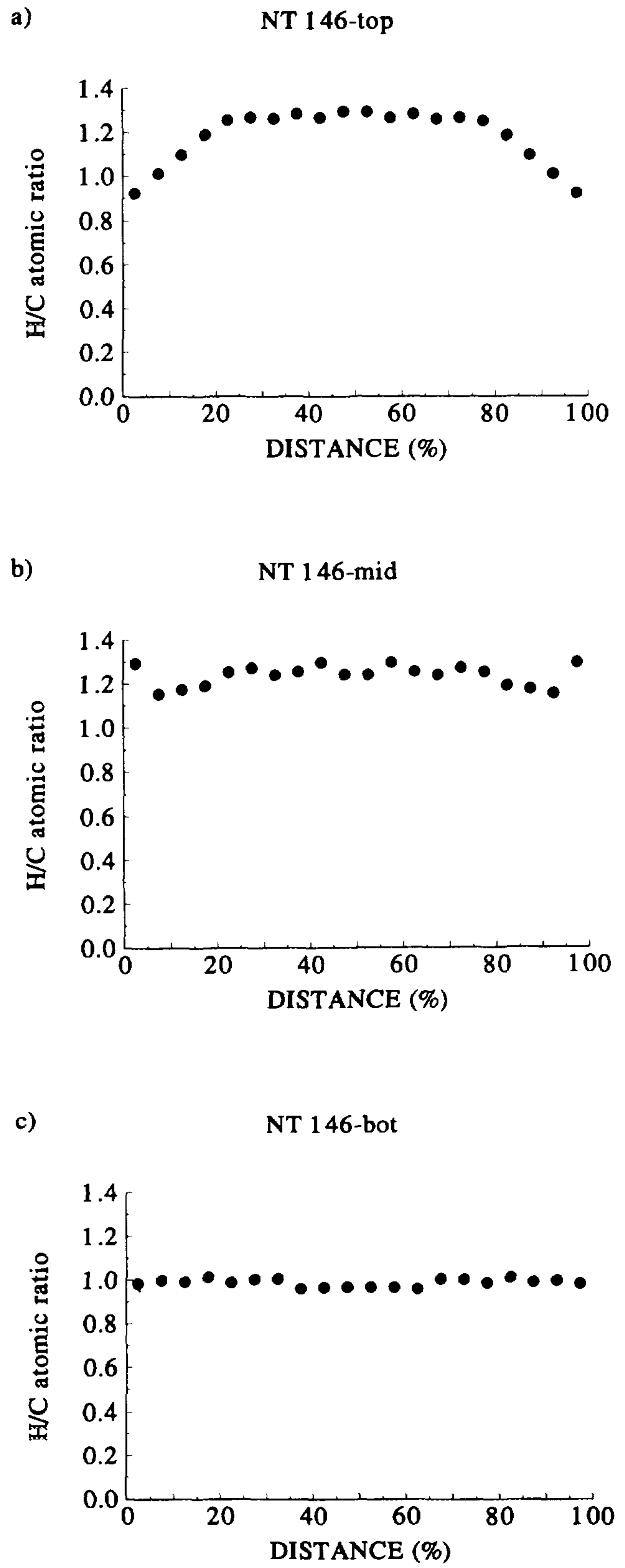

FIG. 8. Spatial variations of hydrogen/carbon atom ratios for TK 771 catalyst exposed in (a) the top (NT 146-top), (b) middle (NT 146-mid) and (c) bottom (NT 146-bot) of a trickle bed reactor.

TABLE 2

Data Used to Calculate Catalyst Pore Filling

	Properties		
Material	Formula	C (g cm^{-3})	Pore volume (cm^3 g^{-1})
Nickel sulphide	NiS	5.5	—
Vanadium sulphide	V_2S_3	4.72	—
Coke	C_2H	1.45[a]	—
Catalysts			
TK 771	—	—	0.5[b]
TK 770	—	—	0.55[b]

[a] Ref. (20).

[b] Average values; these are larger than the specification values.

pellets, and its variation across pellets derived from elemental distributions. However, certain assumptions need to be made concerning the composition and density of the compounds deposited in the pores. The assumptions made in this document are noted in Table 2, with information on pore volumes for the catalysts.

The capacity of the catalysts for foulants can readily be calculated by determining the amounts of vanadium sulphide or coke needed to completely fill the pore volume. The concentration of vanadium and carbon, theoretically present in two catalysts with pores completely blocked with vanadium sulphide or coke, respectively, is noted in Table 3.

In practice, concentrations of carbon and vanadium as high as those indicated in Table 3 have seldom been encountered. The degree of pore filling for the three samples from Run NT146 is more typical and is shown in Fig. 9. The higher near-surface pore filling for NT146-top reflects the high near-surface concentrations of vanadium deposited on the top of the reactor. As the vanadium deposition decreases down the bed, the near-surface blockage of pores decreases. Pore blocking by coke increases down the reactor bed, and the degree of pore filling is similar at pellet surfaces and centres. As can be seen from Fig. 9, the catalyst which has been on stream

TABLE 3

Compositions of Two Catalysts with Pores "Completely" Filled with Coke or Vanadium Sulphide

	Filling Component and Composition of Catalyst	
Catalyst	Vanadium sulphide ≡ V (wt%)	Coke ≡ C (wt%)
TK 771	36.1	40.3
TK 770	37.1	42.6

for 7500 h is not deactivated because of a complete pore blockage by coke and metals deposits, in agreement with Bartholdy and Cooper (16). We do not exclude the possibility of the occurrence of this phenomenon and have found an example of a spent catalyst sample indicating a complete pore blockage, viz., sample CT601-mid. Near-surface pores were effectively blocked, ca. 100% full, as the carbon and vanadium concentrations rose to 3.2 wt% and 32 wt%, respectively. Whilst catalytic activity clearly stops when near-surface pores become completely blocked, access to active sites can be effectively prevented by deposition of much lower amounts of foulants (17). Consequently, the effectiveness of a catalyst may have ceased when the porosity remaining in a pellet is still relatively high because of coke coverage of active sites, and may need to be judged by reactivity tests.

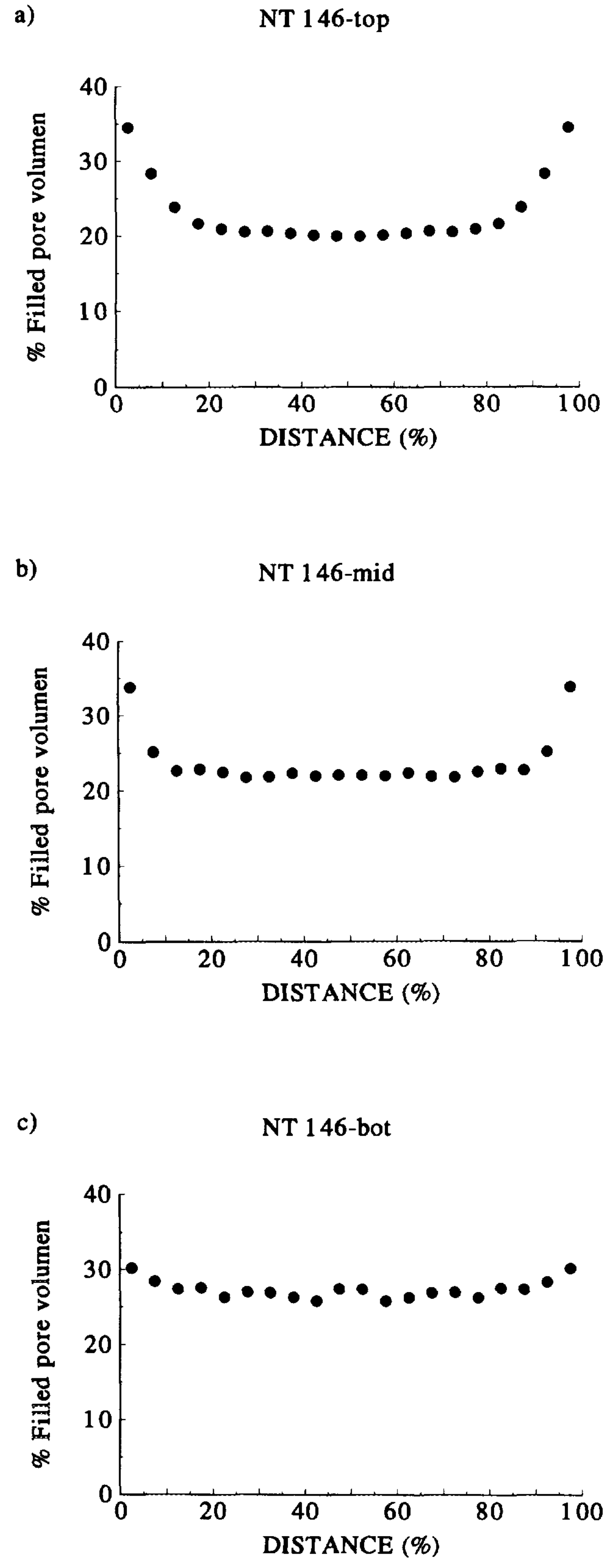

FIG. 9. Distribution of the percentage of filled pore volume across pellets of (a) NT 146-top, (b) NT 146-mid, and (c) NT 146-bot.

4. CONCLUSIONS

Nuclear microprobe methods have been developed which allow the determination of light elements and metallic poisons in used hydrotreating and hydroconversion catalysts. These methods have been applied to study the fouling of catalysts and have provided valuable information on the build-up of coke and its correlation with other foulants. An observation is that the H/C atom ratio of coke falls in regions of catalyst pellets which contain high concentrations of deposited vanadium sulphide. This correlation indicates that hydrogenation is inhibited by the presence of vanadium. Whilst differences have been observed in the rate of movement of carbon, nitrogen, and vanadium into used catalysts, further studies of nitrogen deposition are desirable. The degree of pore filling is readily derived from nuclear microprobe results on catalyst composition and indicates that for some pellets, a value approaching 100% can be reached.

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