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Pyrolysis GC–MS study of external coke composition on H-ZSM-5 zeolite catalysts[1]

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Abstract

The composition of coke formed on the external surface of H-ZSM-5 during the cracking of hexadecane, at 350°C and 20 atm pressure of hydrogen, was analysed using a combination of pyrolysis mass-spectrometry and transmission electron microscopy. It was shown that the external coke consisted of regions of graphite and areas of polyaromatic hydrocarbons. Pyrolysis at a range of temperatures showed cracking products with up to five aromatic rings. Using standard compounds, it was shown that cracking only occurred at exo-cyclic bonds, and therefore we can say that the regions of amorphous coke consist of large polyaromatic molecules linked by saturated hydrocarbon chains. It would appear that these amorphous regions act as precursors to graphitic coke. © 1997 Elsevier Science B.V.

Keywords: Catalyst; Coke; H-ZSM-5; Pyrolysis

1. Introduction

The formation of carbonaceous residues (coke) on hydrocarbon processing catalysts is of considerable technological and economic importance to the petrochemical industry. As a result, a great deal of work has been carried out to study the nature and formation of these deposits. Various analytical techniques have been employed to examine the decomposition of coke on zeolite catalysts and several review articles have been published outlining the methods involved [1–3].

Sorption studies have been used to locate the coke within the pores of the zeolite [4,5], and also to differentiate between the poisoning and blockage of the active sites [6,7]. Bulk techniques such as ^{13}C MAS NMR and FTIR, have been used to investigate the general composition of the coke and to display the change in the coke with reaction temperature [8,9], giving rise to the terms 'high-' and 'low-temperature' coke.

Other bulk analyses, such as, XRD [10], EPR [11,12], and UV–Vis spectroscopy [7], have also been used to study coke deposits. None of these methods are adequate to identify individual components in the coke mixture. However, a solvent extraction technique proposed by Guisnet et al. [13], involving the destruction of the zeolite framework with hydrofluoric acid, has been particularly successful in the study of individual components [1,14–18].

In a previous work [19], we have adapted the technique used by Guisnet et al. to study the coke which is formed within the pores of H-ZSM-5 during the cracking of hexadecane at 350°C under flowing hydrogen. However, a large proportion of the coke was found to be insoluble in methylene chloride and carbon tetrachloride, the solvent used in the dissolu-

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tion of the organic residues. Transmission electron microscopy (TEM) studies [19,20] have shown that the insoluble coke forms cocoons around the external surface of the zeolite crystal, and EDAX analysis has shown that this cocoon remains intact even after the dissolution of the zeolite crystal using 40% HF.

The aim of this work was to investigate the composition and structure of the insoluble coke using a flash pyrolysis technique coupled with GC–MS analysis to complement results achieved using TEM and electron diffraction analyses.

2. Experimental

The sample of ZSM-5 used in this study was supplied by Eka Nobel (Id. No. 13-19-002 EZ-112). Atomic absorption analysis showed the Si/Al ratio of the zeolite to be 70. The zeolite was repeatedly ion-exchanged using ammonium sulphate solution to remove sodium ions from the framework (Na wt%<0.003).

Hexadecane of 99% purity was used without further purification. GC analysis revealed that the major impurities were skeletal isomers of hexadecane.

Prior to reaction, the pelletised catalyst (420-250 μm) was activated at 450°C under flowing hydrogen. The reaction was carried out in a fixed-bed flow reactor (0.5 cm i.d.) at 350°C and 20 atm pressure with pre-dried hydrogen as carrier gas. A ratio of 4/1 : :H_2/feed was maintained for all reactions. The reaction was halted after the required time-on-stream, by turning off the feed. The coked zeolite was then left overnight at the reaction temperature, under flowing hydrogen, to remove any residual products or unreacted feed.

After removal from the reactor, the wt% of carbon and hydrogen on the sample was determined, using a Carlo Erba 1108 elemental analyser.

2.1. Coke analysis

The solvent extraction technique consisted of stirring the coked zeolite with carbon tetrachloride, the catalyst was then separated from the organic phase by filtration and dried. The catalyst was then extracted further using methylene chloride and finally, again after filtering and drying, the zeolite framework was destroyed using 40% HF and the soluble coke was extracted using methylene chloride. The aqueous HF layer was then filtered to collect the residual insoluble coke. Since carbon tetrachloride is too large to enter the pores of ZSM-5, any coke dissolved is assumed to be from the external surface, or in the pore openings. The methylene chloride will then extract any soluble coke accessible to the surface of the zeolite, the final methylene chloride wash after framework destruction will extract any remaining soluble coke. These solvent extracts were concentrated, and quantitatively examined using a GC–MS [19].

The insoluble coke was quantified simply by weighing the filter paper. Several samples of coked zeolite were washed with *N*-methyl-2-pyrrolidone which was found to dissolve the insoluble coke [21]. *N*-Methyl-2-pyrrolidone is too large to enter the pores of ZSM-5, and hence will only remove external coke, it was found that after treatment with *N*-methyl-2-pyrrolidone no insoluble coke could be found using the standard extraction technique. This showed the insoluble coke to be formed solely on the external surface of the zeolite crystals. The insoluble coke was further examined using a Philips EM400 transmission electron microscope fitted with an energy dispersive spectrometer for X-ray analysis (EDAX) system. The insoluble coke from the filter paper was examined and the EDAX used to ensure the complete dissolution of the zeolite framework.

The analysis of the insoluble coke was carried out using an SGE pyrojector II, flash pyrolysis injector (maximum temperature 900°C), connected to a Varian 3400 gas chromatograph which was linked to a Delsi-Nermag (ATI Unicam) Automass 120 mass spectrometer. Helium was used as a carrier gas with a column pressure of 10 psi and an injector pressure of 15 psi. The column used for the analysis was a 5 m × 0.22 mm(i.d.) phenyl deactivated silica capillary column held at 100°C for 2 min, then ramped at 10°C min^{-1} up to 200°C. Approximately 10 μg of sample was used for each pyrolysis. The injector block was held at 300°C to ensure that no coke was condensed on the surfaces. The pyrolysis temperature was varied to alter the degree of fragmentation of the coke and the ionisation potential of the mass spectrometer was altered to reduce fragmentation of pyrolysis products passed onto the mass spectrometer source.

3. Results

In this study, a sample of the external coke from a 100% zeolite catalyst which was on-stream in the reactor for 1 h, was examined. The elemental analysis showed this coked catalyst to have a bulk H/C ratio of 0.2 which shows a highly unsaturated composition (saturated hydrocarbons have a H/C ratio>2). After carrying out the solvent extraction, 95 wt% of the coke on the catalyst was recovered by filtration after HF dissolution and was therefore insoluble, external coke. The sample was found by microanalysis to contain 2 wt% of coke.

The external, insoluble coke was first studied using transmission electron microscopy [19], the complete destruction of the framework was checked using EDAX, and it was evident that the coke formed a cocoon-like structure around the zeolite crystal. Further inspection showed areas of the cocoon to be made up of parallel filaments of the order of 1–2 nm thick which formed twisting sheets on the surface of the cocoon, characteristic of a graphitic structure (Fig. 1). Electron diffraction patterns of these twisting sheets (Fig. 2) were taken and the *d*-spacings for the structure calculated. The observed *d*-spacings and those for graphite are shown in Table 1 and are sufficiently close to assign the structure to that of graphite [22]. Areas of amorphous material, which demonstrated no structure using electron diffraction, were seen between these ordered regions.

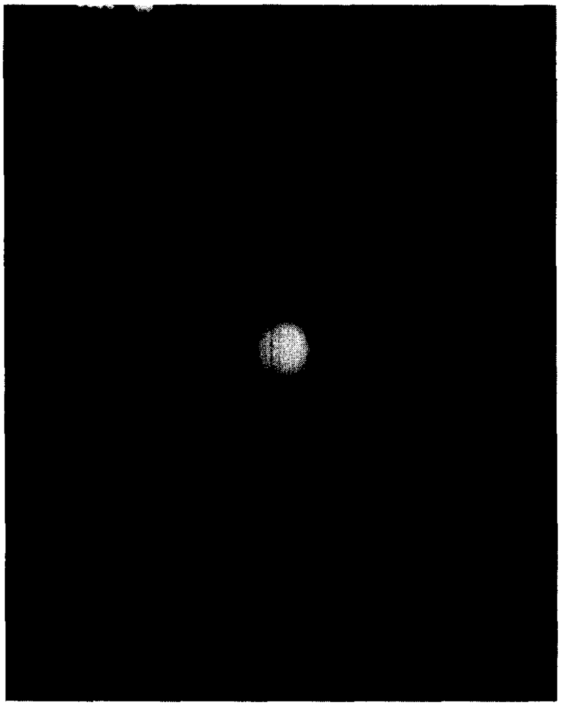


Fig. 2. Electron diffraction pattern of the twisting sheet displayed in Fig. 1.

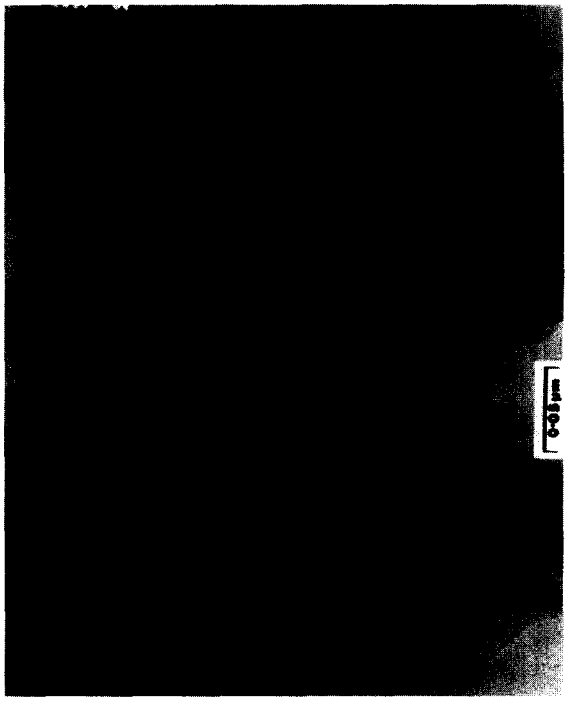


Fig. 1. Twisting sheets observed on the surface of the external coke by TEM analysis.

Initial pyrolysis of the sample was carried out at 900°C with an ionisation potential of 70 eV. The chromatogram (see Fig. 3)shows a crude separation of different components. However, mass spectra over the range of the chromatogram (Table 2) clearly show

Table 1
The observed *d*-spacings from electron diffraction of the twisting sheets observed on the surface of the coke and the theoretical *d*-spacings for graphite

Theoretical *d*-spacing/Å	3.348	2.127	2.027	1.674	1.228	1.113	1.116
Observed *d*-spacing/Å	3.334	2.096	1.982	1.667	1.222	1.118	1.112

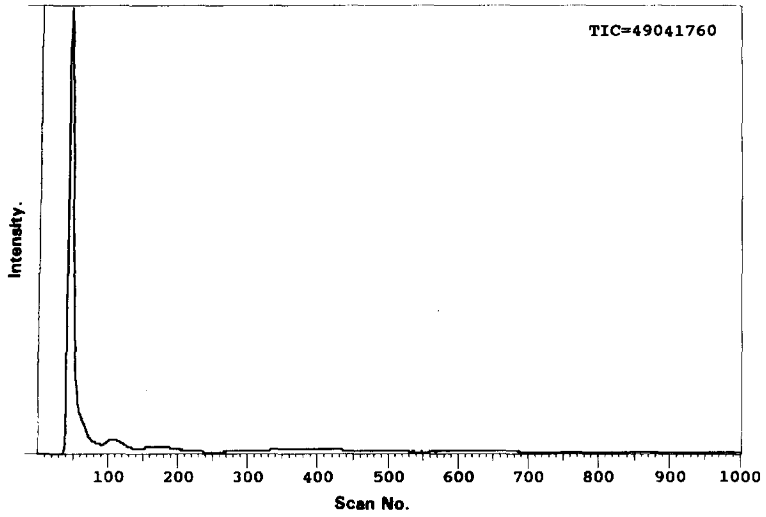


Fig. 3. The chromatogram of products from the external coke of the zeolite pyrolysed at 900°C with an ionisation voltage of 70 eV.

Table 2
The products from the external coke of the zeolite pyrolysed at 900°C with an ionisation potential of 70 eV

M.W.T.	Retention time (m : s)	Identification	Formula	No. of rings
92	11.6	Toluene	C_7H_8	1
116	11.87	Indene	C_9H_8	2
128	12.15	Naphthalene	$C_{10}H_8$	2
142	12.97	Methyl-naphthalene	$C_{11}H_{10}$	2
154	13.52	Biphenyl	$C_{12}H_{10}$	2
152	14.95	Acenaphthylene	$C_{12}H_8$	3
168	16.65	Phenyl-toluene	$C_{13}H_{12}$	2
182	17.15	Dimethyl-biphenyl	$C_{14}H_{14}$	2
180	21.43	Methyl-fluorene	$C_{14}H_{12}$	3
194	23.58	Ethyl-fluorene	$C_{15}H_{14}$	3
178	24.67	Anthracene/phenanthrene	$C_{14}H_{10}$	3
192	25.17	Methyl-anth/phen	$C_{15}H_{12}$	3
206	1 : 01.55	Dimethyl-anth/phen	$C_{16}H_{14}$	3
202	1 : 06.98	Pyrene	$C_{16}H_{10}$	4
220	1 : 18.96	Trimethyl-anth/phen	$C_{17}H_{16}$	3
216	2 : 22.97	Methyl-pyrene	$C_{17}H_{12}$	4
230	3 : 26.27	Dimethyl-pyrene	$C_{18}H_{14}$	4
228	4 : 41.27	Chrysene	$C_{18}H_{12}$	4
242	5 : 29.07	Methyl-chrysene	$C_{19}H_{14}$	4

the composition of the various pyrolysis products changing with time. Further pyrolysis was carried out at 600°C, and again at 900°C, with an ionisation potential of 45 eV. The retention times, parent ions (molecular weight) and assigned structure of each component are given in Tables 2–4.

From Table 2, we can see that a range of aromatic and polyaromatic compounds were detected in the pyrolysed coke, up to a molecular weight of 242, with a maximum of four aromatic rings. Table 3 shows that the reduction of the pyrolysis temperature to 600°C, as expected, reduced the number of pyrolysed products

Table 3
The products from the external coke of the zeolite pyrolysed at 600°C with an ionisation potential of 70 eV

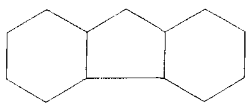
M.W.T.	Retention time (m : s)	Identification	Formula	No. of rings
92	13.57	Tolune	C_7H_8	1
128	14.67	Naphthalene	$C_{10}H_8$	2
142	17.09	Methyl-naphthalene	$C_{11}H_{10}$	2
152	17.36	Acenaphthylene	$C_{12}H_8$	3
178	29.29	Anthracene/phenanthrene	$C_{14}H_{10}$	3
192	48.90	Methyl-anth/phen	$C_{15}H_{12}$	3
206	1 : 22.42	Dimethyl-anth/phen	$C_{16}H_{14}$	3
202	2 : 17.31	Pyrene	$C_{16}H_{10}$	4
220	2 : 31.76	Trimethyl-anth/phen	$C_{17}H_{16}$	3
216	4 : 0.05	Methyl-pyrene	$C_{17}H_{12}$	4

Table 4
The products from the external coke of the zeolite pyrolysed at 900°C with an ionisation potential of 45 eV

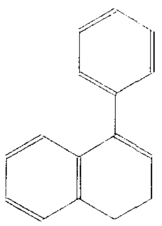
M.W.T.	Retention time (m : s)	Identification	Formula	No. of rings
92	12.58	Toluene	C_7H_8	1
128	13.38	Naphthalene	$C_{10}H_8$	2
142	13.96	Methyl-naphthalene	$C_{11}H_{10}$	2
152	14.83	Acenaphthylene	$C_{12}H_8$	3
168	15.60	Phenyl-toluene	$C_{13}H_{12}$	2
166	18.63	Fluorene	$C_{13}H_{10}$	3
182	19.18	Dimethyl-biphenyl	$C_{14}H_{14}$	2
180	21.43	Methyl-fluorene	$C_{14}H_{12}$	3
178	24.83	Anthracene/phenanthrene	$C_{14}H_{10}$	3
192	35.22	Methyl-anth/phen	$C_{15}H_{12}$	3
206	1 : 02.14	Dimethyl-anth/phen	$C_{16}H_{14}$	3
202	1 : 22.09	Pyrene	$C_{16}H_{10}$	4
220	2 : 11.26	Trimethyl-anth/phen	$C_{17}H_{16}$	3
216	2 : 17.80	Methyl-pyrene	$C_{17}H_{12}$	4
230	2 : 57.75	Dimethyl-pyrene	$C_{18}H_{14}$	4
244	3 : 37.36	Benzyl-biphenyl	$C_{19}H_{16}$	3
256	3 : 45.22	Dimethyl-benzophenathrene	$C_{20}H_{16}$	4
252	3 : 50.93	Benzopyrene	$C_{20}H_{12}$	5
266	4 : 33.63	Benz [j] aceanthrylene-3-methyl	$C_{21}H_{14}$	5

although some four-ring compounds were still detected up to a molecular weight of 216. When the higher pyrolysis temperature was used and the ionisation potential dropped to 45 eV, a distribution similar to that at 70 eV was obtained; however, some five-ring products were observed and the highest molecular weight was 266.

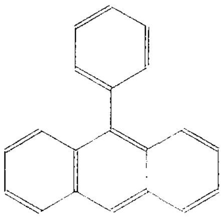
Three standard samples, 9-phenyl-anthracene, perhydrofluorene and 1-phenyl-3,4-dihydronaphthalene (Fig. 4) were pyrolysed at 900°C and 70 eV to show the bonds which are broken under these conditions. The chromatograms for 9-phenyl-anthracene and 1-phenyl-3,4-dihydronaphthalene are shown in Figs. 5 and 6, we can see that in the case of the 9-phenyl-anthracene, 25% of the compound (peak A) is pyrolysed to give anthracene (peak B) and benzene (peak C). In the case of the 1-phenyl-3,4-dihydronaphthalene (peak A), 50% is pyrolysed to give a mixture of naphthalene and benzene (peak B). Selective ion monitoring of peak B (Fig. 7) shows an approximately 1 : 1 ratio of naphthalene and benzene which we would expect from the cracking of the dihydronaphthalene-phenyl bond, however the major ion in the mass spectrum of peak A (Fig. 8) was 204



Perhydrofluorene
M.W.T. = 178



1-Phenyl-3,4-dihydronaphthalene
M.W.T. = 206



9-Phenylanthracene
M.W.T. = 254

Fig. 4. The structures of the three standard compounds used to test the pyrolysis conditions.

(M.W.T.=206). Coupled with the presence of naphthalene, rather than dihydronaphthalene in the cracking products, this shows that the dehydrogenation of the saturated bond in the dihydronaphthalene, while giving a more stable aromatic species, is a major reaction step in pyrolysis at this temperature. The perhydrofluorene is totally pyrolysed to give a mixture of cracking products.

4. Discussion

It would appear that the cocoon on the outer surface of the coked zeolite crystal consists of two regions: firstly, the previously reported graphite regions [19], and secondly, large areas of highly unsaturated polyaromatics. These polyaromatics are cracked at 900°C to give a range of aromatic products with up to five aromatic rings.

We have shown, by using the three test compounds, that single carbon–carbon bonds can be cracked at 900°C; however, not all the single carbon–carbon bonds are broken and the double bonds remain intact under these conditions. It seems likely therefore that the amorphous regions consist of extremely high molecular weight hydrocarbon molecules which appear to contain regions of aromaticity, with some saturated bonds at which cracking can occur. These regions would appear to be the precursors to the

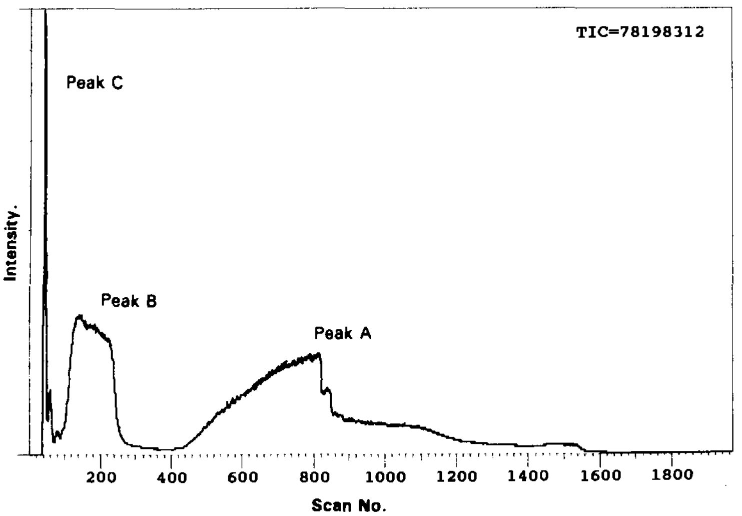


Fig. 5. Chromatogram of 9-phenylanthracene pyrolysed at 900°C with an ionisation voltage of 70 eV.

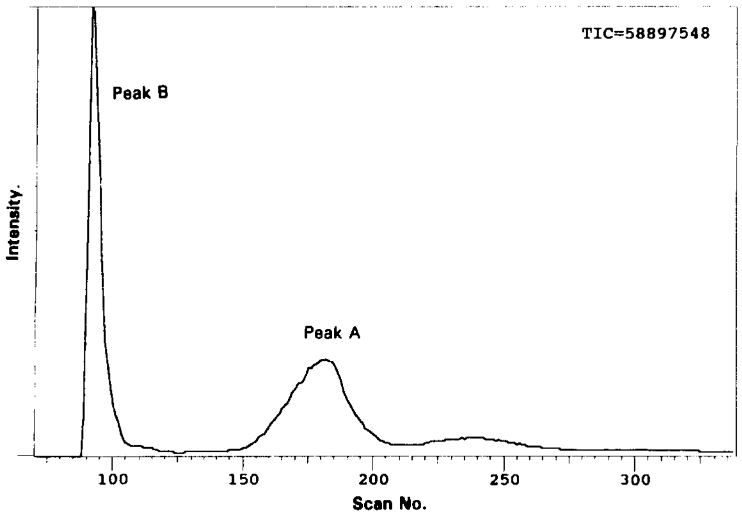


Fig. 6. Chromatogram of 1-phenyl-3,4-dihydronaphthalene pyrolysed at 900°C with an ionisation voltage of 70 eV.

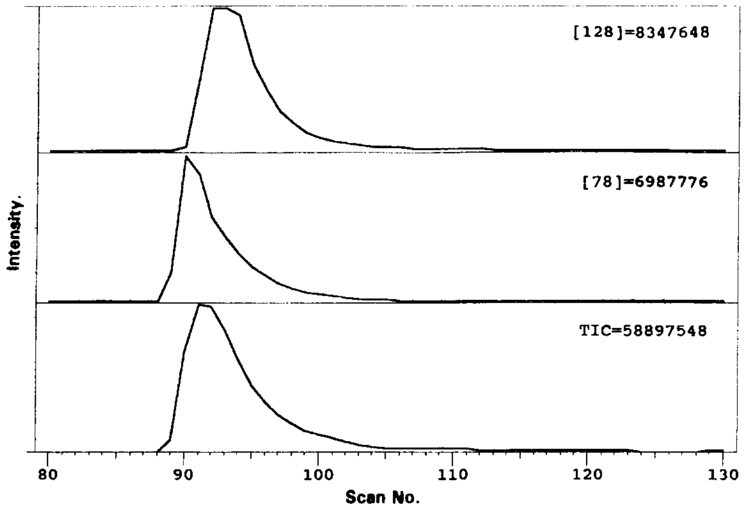


Fig. 7. Selective ion monitoring of peak B in Fig. 6 showing the similar concentrations of benzene and naphthalene.

formation of the graphitic structure and the level of unsaturation is a function of the reaction time. The presence of the one- and two-ring aromatics shows that areas of relatively saturated coke are present in the cocoon, since we have shown that these conditions do not break double bonds. This is also shown by the large number of methyl substituted products which can only be formed by the presence of saturated carbon chains. The fragmentation of these large hydrocarbons would seem to occur at exo-cyclic carbon–carbon single bonds since the dihydronaphthalene was almost completely dehydrogenated to give naphthalene prior to the cracking of the exocyclic bond, no evidence of cracking of the saturated cyclic bond was found.

The test compounds also illustrate that not all single carbon–carbon bonds are broken by pyrolysis at this temperature. It is therefore likely that not all of the amorphous coke was pyrolysed, and that much larger polyaromatic compounds are present.

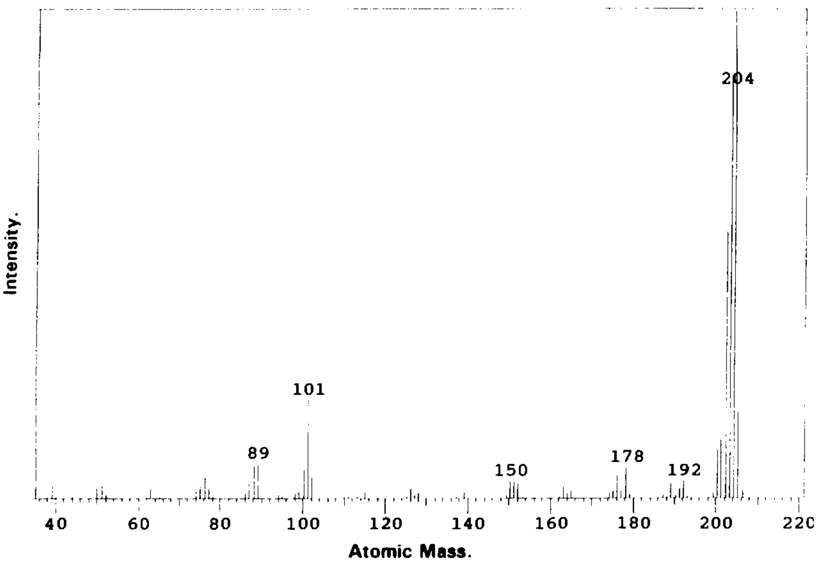


Fig. 8. The mass spectrum of peak A in Fig. 6 showing the dominant ion to be 204, the dehydrogenated compound.

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