

CHROM. 5722

Gas chromatography of the coke formed in catalytic cracking reactions

There have been several research reports regarding the formation of coke, the amount of coke on the catalyst and the relative coking ability of the various hydrocarbons. THOMAS¹ managed to extract 27% of the deposit formed by the passage of *n*-octenes over an alumina-zirconia-silica catalyst at 375° and at about 8 atm with benzene. Part of the extract (40%) was soluble in acetone and was a dark oil. The remaining portion of the extract, insoluble in acetone, was a dark solid melting at 195° to 210°. Hydrogen to carbon ratios were different for the two portions of the extract. Under standardized cracking conditions different amounts of coke are formed from various hydrocarbons. The relative amounts of coke formed from various hydrocarbons under constant conditions are given by VOGÉ *et al.*². Using a radioactive tracer technique McMAHON³ concluded that all carbon atoms take part, with equal facility, in coke formation when cracking *n*-heptane. The same thing was also observed with *n*-octane and *n*-octene. MELIK-ZADE *et al.*⁴⁻⁶ observed the formation of coke by passing ¹⁴C-labelled *n*-pentylbenzene over a catalyst both alone and in *n*-hexadecane. Their observations indicated that most of the coke was formed from the reaction with the *n*-pentyl group and the contribution of the benzene ring to the formation of coke was very low. HIGHTOWER AND EMMETT⁷ by using radioactive tracers have concluded that the olefins are the most active compounds in forming coke. Alkyl aromatics, benzene and paraffins follow olefins in the order given in their ability to form coke.

There are practically no reports in the literature describing the analysis of coke. If the various hydrocarbons differ in their ability to form coke it seems probable that the coke formed from them will have a different composition and that this composition may also change even for the same hydrocarbon if the cracking conditions vary. With this in mind, an analytical study of coke formed in the catalytic cracking of *n*-pentane and isopentane was carried out and the results obtained on the gas chromatography of the coke are now presented.

Experimental

The experimental set-up is similar to the usual apparatus for catalytic hydrocarbon (vapour) cracking and consists of a helium carrier gas supply, a hydrocarbon bubble saturator, a Pyrex glass reactor mounted vertically containing 25 g of Davison-980 Si-Al catalyst (7-10 mesh). The reactor is placed in a furnace in which a temperature of $518 \pm 1^\circ$ is maintained by a temperature controller. The apparatus also contains a catalyst regeneration system in which the catalyst is regenerated by passing water vapour and air through it at 520°. A stream of helium at a pressure of one atmosphere saturated with hydrocarbon vapour passes at a rate of 40 ml/min through the catalyst. The gas emerging from the reactor could be injected into the gas chromatograph, by means of a by-pass system, and analysed. After the hydrocarbon vapour had been passed over the catalyst for 1 h, the saturator was by-passed and the helium flow continued through the reactor to remove any adsorbed, unabsorbed and uncoked by-products. At the same time the heating current was turned off. After the reactor had cooled down it was disconnected from the system and the catalyst with its coke deposit was taken out and was placed in pure acetone in a bottle overnight. After

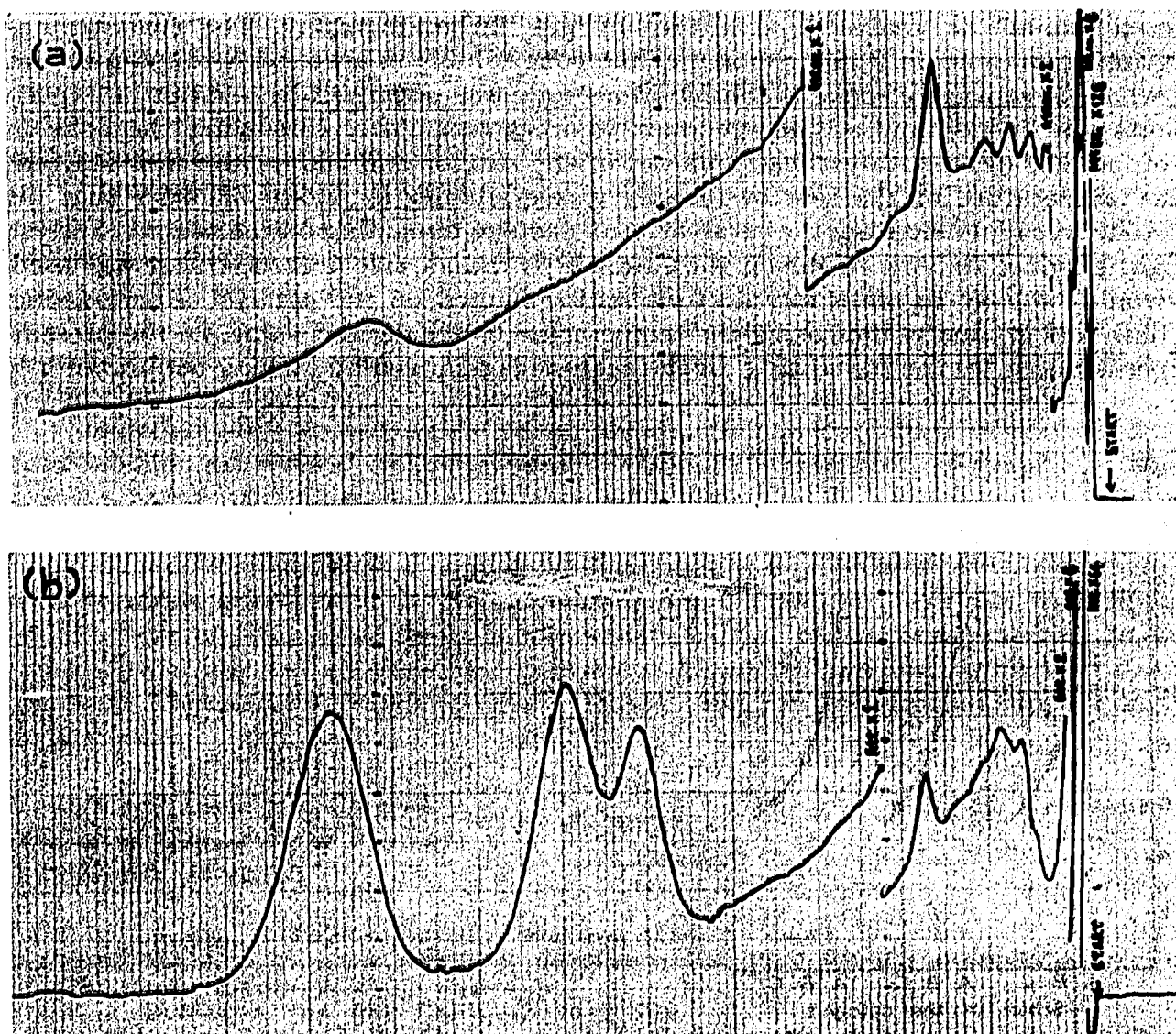


Fig. 1. Analysis of (a) coke formed in *n*-pentane cracking and (b) coke formed in isopentane cracking. Column: 6 ft. \times $\frac{1}{4}$ in., 20% SE-30 on Chromosorb; temperature, 260°; flame ionization detector.

filtering this, a clear brownish yellow solution of coke dissolved in acetone was obtained. Coke solutions obtained in this manner from several runs were collected together. A concentrated solution of coke in acetone was injected into a gas chromatograph for analysis.

Fig. 1a shows a chromatogram obtained from a coke solution, the coke being obtained by cracking *n*-pentane. Fig. 1b is a similar chromatogram obtained with isopentane coke. Obviously the two chromatograms show some differences. A first conclusion from this analysis is that coke obtained from different compounds differs in composition. The conditions of cracking were controlled during all runs. It was assumed, therefore, that coke obtained in various runs for the same hydrocarbon cracking had a constant composition. The yields of coke from different runs were collected together since a very small amount of coke is obtained in an individual

run it cannot be analysed separately by gas chromatography. The two chromatograms represent only that portion of the coke soluble in acetone. A rough measure of what percentage of coke is soluble in acetone was obtained by a series of experiments with *n*-pentane as the specimen hydrocarbon. After dissolving the coke in acetone, the dried catalyst was replaced in the reactor and the helium flow started. The temperature of the reactor furnace was gradually increased in order that all acetone was removed from the catalyst. Any acetone remaining on the heated catalyst might produce its own effects on the catalyst. If radioactive acetone tracer was used it would be easy to see if any acetone still remained on the catalyst after passing helium and gradually increasing the temperature to the desired value. In the present experiments it was assumed that all the acetone is removed by passing helium for 1 h

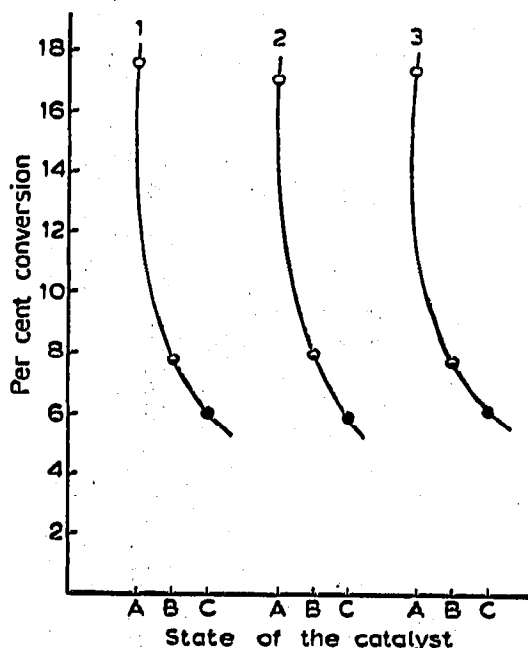


Fig. 2. Effect of dissolving coke from catalyst by acetone on the activity of catalyst. ○, Regenerated catalyst; ◐, catalyst from which coke is dissolved; ●, lowest activity when coke is completely deposited on catalyst. The upper two points are after 4 min from start. State of the catalyst: A = regenerated catalyst, B = catalyst from which coke is dissolved, and C = catalyst completely covered with coke.

and gradually increasing the temperature. The catalyst was maintained at $514 \pm 1^\circ$ and the activity of it for *n*-pentane cracking measured at 4 min and 12 min after *n*-pentane vapour started, and continued until constant activity was obtained. In the next run the catalyst was regenerated by passage of water vapour and air over the catalyst at 520° for one day and the activity of this regenerated catalyst was measured at the same intervals of time. These two experiments were repeated several times. Activity is given in terms of per cent conversion of *n*-pentane. Per cent conversion was calculated by determining the amount of *n*-pentane before and after cracking. This was done by measuring the height of *n*-pentane peaks before and after cracking.

$$\text{Per cent conversion} = \frac{\text{decrease in partial pressure of } n\text{-pentane}}{\text{original partial pressure of } n\text{-pentane}} \times 100$$

Fig. 2 represents the data from several experiments under these two conditions. Every curve shows three points. The empty circles represent the values obtained with regenerated catalyst, half solid circles indicate the values with catalyst from which coke has been removed by acetone and the solid circles represent the constant lowest value of per cent conversion obtainable at the end of every run.

During the regeneration process activity is raised from the value at the lowest point to the value at the highest point. If we assume that by this regeneration process recovery of activity is 100% (*i.e.* all coke is removed from the catalyst), the recovery of activity by the use of acetone (corresponding to middle points) could be calculated from the per cent conversion values at the three points. It was found that an increase in activity of approximately 16% takes place after using acetone. A rough estimate is therefore that only 16% of coke is dissolved in the acetone.

Further work on naming the compounds in coke and the study of coke obtained from olefins, aromatics, etc. is proposed. The thin layer chromatography of these cokes is being carried out.

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