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GAS CHROMATOGRAPHIC STUDIES OF CATALYSIS ON Ni–SiO$_2$

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SUMMARY

The hydrocracking of paraffin hydrocarbons on a Ni–SiO$_2$ surface is studied using a variety of gas chromatographic techniques including elution, elution with reaction, stopped-flow, and sample-vacancy chromatography. The results demonstrate the kinds of information about catalytic reactions which can be provided by each technique, and reveal new features about the nature of the hydrocracking reaction itself.

INTRODUCTION

In previous papers[1-3] we have described how various gas chromatographic techniques can be useful in the general study of catalysis and in particular heterogeneous catalytic reactions involving hydrocarbons. We are now engaged in a detailed study of one particular catalyst, namely Ni supported on SiO$_2$, and this paper outlines the results obtained so far, most of which are concerned with the hydrocracking reaction[4-7]. In our experience this has had a particularly simple overall chemistry involving the cleavage of a terminal carbon atom from an alkane chain to give CH$_4$ and the next lower alkane. The experiments reveal new features of the catalytic reaction, demonstrate the interplay of the various chromatographic techniques, and have led to a number of developments of these chromatographic techniques.

EXPERIMENTAL

All the chromatographic work has been carried out using Pye 104 gas chromatographs with flame ionisation or thermal conductivity detectors where appropriate, and for the most part using 1.5 m × 3 mm glass columns fitted with glass–metal seals at their outlets. The catalyst is prepared by slurrying the silica support with a 0.05 M aqueous solution of nickel nitrate and evaporating to dryness under vacuum with gentle heating and constant agitation. Sufficient nickel nitrate is employed to give a catalyst with 2.3–2.7 % (w/w) of nickel. The dry material is packed into the columns and reduced in a current of hydrogen (20 ml/min) at 350° for 3 h. Porasil of A, B or C grades (80–100 mesh) has been used as the silica support. While all the Porasil A particles become coated with nickel using this procedure, this is true of only a propor-

tion of Porasil B or C, suggesting that these may act as mixtures of A with material of lower surface activity. Catalysts made with the two latter grades have a speckled appearance, but significant differences of behaviour have not been observed between catalysts prepared from the different grades. All the catalysts suffer changes in specific activity towards the reactions studied and generally become of lower activity with time. They can be partially reactivated by treatment at 350° with hydrogen or a hydrogen–air mixture.

Since small traces of oxygen in the carrier gas through the catalytic columns can (as we have amply demonstrated experimentally) often have a significant effect on the catalyst and the reactions studied, the carrier gases are freed from oxygen with manganese oxide supported on Celite as we have described elsewhere[8]. In order to prevent oxygen being admitted to the catalyst as a result of an injection of substances into the chromatograph, a short length of the column at the inlet may be packed with supported manganese oxide separated from the catalyst by a plug of glass wool. In this case, a small correction becomes necessary for the residence times of hydrocarbons on this material.

In sample-vacancy chromatography with adsorbable vapours and especially when there is a considerable pressure drop across the reactor column, we have found it necessary to equalise the pressure in the injection valve[9] with that at the injection point between the catalyst and analytical columns. If this is not done errors can arise due to desorption of vapours from the valve and injection loop.

We have found that the most satisfactory method of calibrating the volume of the injection loop is to determine the detector response to a continuous feed of hydrocarbon at a measured flow-rate, and then to measure the signals obtained when loop injections are made of the same hydrocarbon feed gas at different filling pressures. The response to the continuous feed can be determined most easily by substituting a loop of large volume for the normal injection loop so as to produce a "square-wave" signal. Using this method the sample loop is compared with the device used for measurement of flow-rate. Other methods of sample-loop calibration, such as comparison of signals obtained from the loop and from syringe injection of the same gas mixture, give the same results but significant corrections have to be made for adsorption in the syringe and for injection leakage.

ELUTION CHROMATOGRAPHY

Information about the Ni–SiO$_2$ catalyst surface can be obtained from the elution chromatography of alkanes, particularly if the experiments are carried out at temperatures below about 170° in hydrogen carrier gas, under which conditions the hydrocracking reaction is very slow indeed. Above this temperature, the chromatograms are confused with products and the shape of the elution profile of the reactant may be distorted. While symmetrical peaks are obtained on Porasil alone up to quite large sample sizes (e.g. using our column dimensions 3 × 10^{-4} g of hexane at 174°), they are only obtained from Ni–SiO$_2$ columns with very small samples (e.g. not more than 3 × 10^{-8} g of hexane). This reflects the smaller area of the nickel surface, the variation of heat of adsorption with surface coverage, and the greater retention times. Thus 3 × 10^{-8} g. of hexane is eluted symmetrically from Porasil C at 174° in 1.04 column dead volumes and from Ni–Porasil C in 2.02 dead volumes.
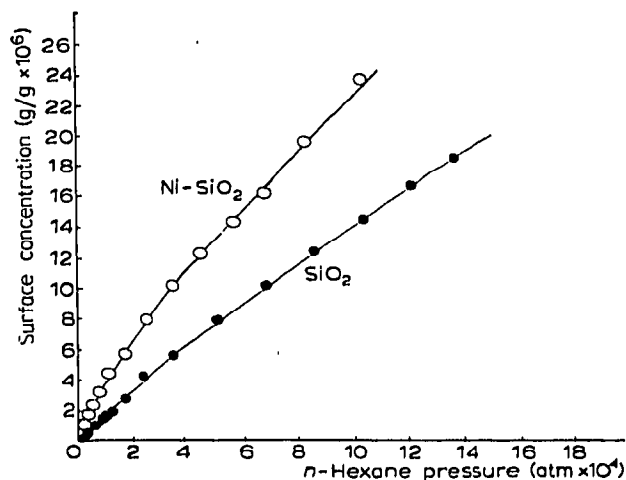
Fig. 1. Adsorption isotherms for *n*-hexane on Ni–SiO₂ and SiO₂ at 100° under hydrogen.

From the asymmetric peaks obtained when the sample size exceeds the above values it is possible to calculate the adsorption isotherms, for example using the simple method of Huber and Keulemans[10]. Fig. 1 illustrates the type of result obtained using, however, linear scales which only show a small portion of the full range of the isotherm which is measured: the difference between the catalyst and the support alone is clearly demonstrated. Heats of adsorption are determined from the temperature variation of these isotherms. On Porasil alone, this heat is effectively constant over a wide range (*e.g.* for hexane at 29.5 kJ/mol for surface concentrations over the range 10^{-7}–10^{-4} g/g), but on Ni–Porasil the heat of adsorption (hydrogen carrier gas) falls continuously with increasing surface coverage (*e.g.* for hexane from 44.0 to 32.0 kJ/mol over the same range). The isotherms on Porasil have an interesting feature in that they are essentially linear over a large range of pressures, but at very low pressures of adsorbate the gradient increases and the isotherm drops sharply to zero. (This does not feature in Fig. 1 because of the scale chosen.) The chromatographic consequence of this is that symmetrical peaks are observed at relatively large sample sizes, but these have very thin "tails", which would be unnoticed in many normal chromatographic applications.

Where the retention of substances by the catalyst is large enough (*i.e.* at sufficiently low temperatures) it is possible to titrate the surface by repeated injections of the adsorbate, the end-point being determined from the emergence of the adsorbate as distinct peaks which then rapidly increase in size to a constant value corresponding to no further significant adsorption. This has been carried out on the Ni–SiO₂ catalysts for example with hydrogen, oxygen, and carbon monoxide[11]. Assuming that each H₂, O₂ or CO molecule occupies 2 adsorption sites on a (100) plane of the fcc structure of nickel, one obtains thus for a fresh catalyst specific areas of 64 (H₂), 64 (O₂) and 53 (CO) m² per gram of nickel. It has also been observed that the titration values depend very much on the history of the reactor column. Thus the value drops by a factor of 10 or more when the catalyst has experienced extensive treatment with hydrocarbons. For a column previously heated in a stream of nitrogen overnight at 350°,

the subsequent hydrogen titre can be recovered by temperature-programming the column, most of it eluting below 300°. An attractive approach to the determination of the amount of exchangeable hydrogen on the catalyst surface is the measurement of the retention time of deuterium using hydrogen carrier gas[12-14].

ELUTION CHROMATOGRAPHY WITH REACTION ON THE COLUMN

(a) With hydrogen as carrier gas, olefins and acetylenes are so rapidly hydrogenated that no useful kinetic information can be obtained from most chromatograms, which are merely identical with those produced by injection of the corresponding saturated hydrocarbons. However aromatics (e.g. benzene at 80°) react sufficiently slowly for a kinetic analysis to be made from the reaction chromatogram. The supporting SiO_2 acts as an efficient elimination catalyst[15] in such reactions as

$$RCl\ (ROH,\ RNH_2\ etc.) \rightarrow Olefins + HCl\ (H_2O,\ NH_3,\ etc.).$$

The subsequent rapid hydrogenation of the olefins on $Ni-SiO_2$ under hydrogen is sometimes useful in the study of these reactions as secondary reactions (such as olefin polymerisation) may thus be avoided.

(b) Injection of alkanes with hydrogen as carrier gas and at temperatures above 170° leads to considerable hydrocracking. Fig. 2 illustrates the particular case of a chromatogram obtained at a temperature where the reaction rate is still very small. The shape of the methane step indicates that there is uniform activity along the catalyst column; measurement of the constancy of the step height under such conditions provides a useful method for testing the reactor or catalyst uniformity. The two small steps in Fig. 2 in front of the decane peak correspond to the nonane and octane products displaced from the column by the decane. Because of the sequential nature of the reaction, that is a C_r hydrocarbon yields only a C_{r-1} hydrocarbon and CH_4, it is surprising that the octane step is as large as it is. This may arise from the displace-
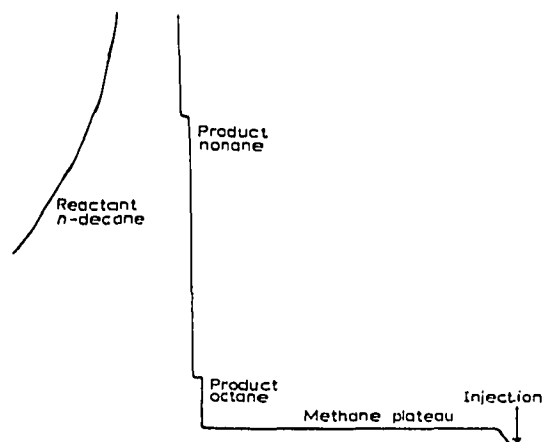

Fig. 2. Reaction chromatogram for the hydrocracking of n-decane on $Ni-SiO_2$ under hydrogen at 176°.

ment of hydrogen from the surface at the hydrocarbon front, so that reaction occurs predominantly at this front where there is an accumulation of nonane.

(c) The hydrocracking reaction may also be studied in the reverse manner, that is by injecting samples of hydrogen into nitrogen carrier gas with hydrocarbon either adsorbed previously onto the column or supplied as a continuous stream in the nitrogen. With e.g. n-octane at 192° there is almost complete conversion of all the hydrogen to CH_4: this allows a Ni–SiO₂ catalyst to be used in conjunction with a flame ionisation detector to estimate very small amounts of hydrogen. Alternatively using hydrogen carrier gas it could serve as the basis of a quantitative carbon detector by complete conversion of all carbon-containing molecules to CH_4.

It is of some interest to note that with squalane on the column at 200°, very little methane is produced and the reaction is less than 1 % complete under the conditions (above) when n-octane is virtually 100 % reacted. Pure squalane (2,6,10,15,19,23-hexamethyltetracosane) should have no terminal $-CH_2CH_3$ groups and thus should give little hydrocracking at these temperatures (see Microcatalytic technique with stopped-flow).

STOPPED-FLOW CHROMATOGRAPHY

In stopped-flow chromatography[2], the gas flow through the chromatographic column in which a reaction is occurring is stopped from time to time so that the chromatography is then switched off while the reaction continues. The reaction products formed during each stop produce individual sharp chromatograms from which a great deal more detail about the reaction may be extracted than from straightforward elution chromatography with reaction. The elimination plus hydrogenation reactions mentioned in the previous section under (a) readily lend themselves to this technique. A further example of a reaction on the Ni–SiO₂ surface which we have studied in this way is the Fischer–Tropsch reduction[11] of CO by H_2 to give CH_4. CO is injected on to the catalyst column under hydrogen and is strongly adsorbed so that it remains virtually stationary on the column while it is steadily reduced to methane (e.g. at 100–200°). The reaction rate rises initially and then after some time falls off with simple first-order kinetics. (It will eventually fall to a low plateau value unless great care is taken to remove traces of CO from the hydrogen!) The initial part of the reaction probably corresponds to self-poisoning of the reaction by CO.

The hydrocracking of e.g. n-dodecane as illustrated in Fig. 2 could also be studied with stopped-flow chromatography, but the technique becomes more and more informative with increase in the retention time of the reactant, i.e. for alkanes containing 15 or more carbon atoms, and gives correspondingly very little information with smaller hydrocarbons.

MICROCATALYTIC TECHNIQUE WITH STOPPED-FLOW

We therefore decided to investigate the hydrocracking reaction with what may be regarded as a modification of the classical technique of Kokes et al.[16] in which a small reactor column is followed by an analytical gas chromatographic column which separates the products from a pulse of reactant passed rapidly through the reactor. In our experiments the reactant, e.g. n-dodecane, was passed on to the reactor column
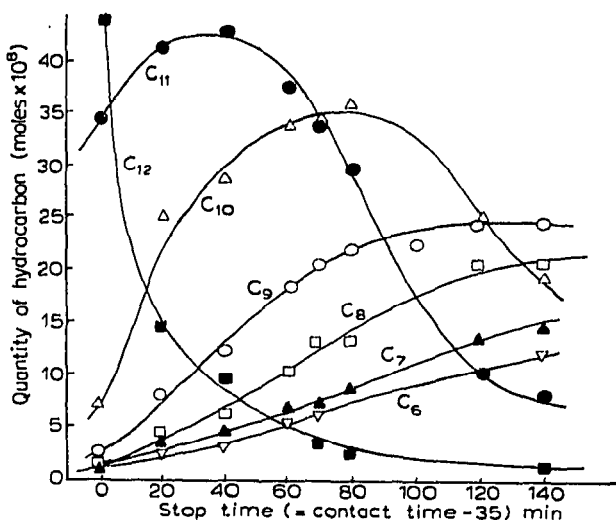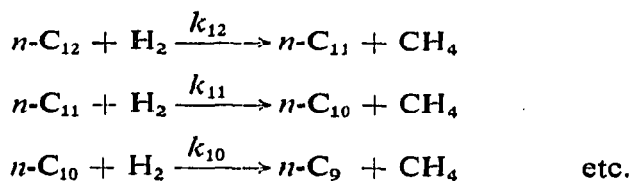
Fig. 3. The progressive hydrocracking of *n*-dodecane on Ni–SiO₂ at 177° under hydrogen, using the stopped-flow microcatalytic technique. C_r = Straight-chain alkane with r carbon atoms.

in hydrogen and the gas flow stopped for an interval which was varied from experiment to experiment. The reactant plus products were eluted on to a trap and then passed to a gas chromatographic column where they were analysed by temperature programming. In this way the exact contact time on the catalyst surface was known. Fig. 3 shows a typical plot of the analytical results for dodecane hydrocracking on Ni–SiO₂ at 177°.

The reaction was found to follow the following sequence:

$$n\text{-}C_{12} + H_2 \xrightarrow{\quad k_{12} \quad} n\text{-}C_{11} + CH_4$$

$$n\text{-}C_{11} + H_2 \xrightarrow{\quad k_{11} \quad} n\text{-}C_{10} + CH_4$$

$$n\text{-}C_{10} + H_2 \xrightarrow{\quad k_{10} \quad} n\text{-}C_9 + CH_4 \qquad \text{etc.}$$

There seems to be little variation between the various velocity constants, k_{12}, k_{11}, k_{10} etc. Each reaction follows excellent first-order kinetics, although this may merely reflect the fact that the total number of reactant hydrocarbon molecules stays constant throughout the experiment. Calculation shows that there is no significant hydrocarbon loss to the catalyst to form non-volatile products, a result which is in contrast to experiments under nitrogen described in the next section. Assuming the rate constants for each successive reaction to be the same, a simple kinetic analysis shows that the maximum concentration of a C_r hydrocarbon should occur when the concentration of the C_r hydrocarbon is equal to the concentration of the C_{r+1} hydrocarbon. Further the maximum concentrations of the successive hydrocarbons should be separated by equal intervals of time. These expectations are fairly closely fulfilled by the experimental results.

One of the most astonishing features of these hydrocracking reactions is the

TABLE I

EFFECT OF TEMPERATURE ON HYDROCRACKING REACTIONS ON Ni-SiO₂

Reactant	Temperature for $k = 10^{-2} min^{-1}$ (°C)	Change in rate for 10°	Activation energy $(kJ \cdot mol^{-1})$
n-Dodecane	174	×8.4	392
2,3-Dimethylbutane	215	×4.6	296
Ethyl cyclohexane	163	×5.3	305
Cyclohexane (ring opening)	219	×21	556

very high values found for the activation energies. Some data are collected in Table I.

Alkanes containing $-CH_2-CH_3$ groups switch on at the lowest temperatures, then those containing $>CH-CH_3$ groups and finally there is an opening of C_5 and C_6 rings. These distinctions could be used to distinguish hydrocarbons of different types. The hydrocracking reaction could also provide a clean method of preparing compounds with one (or two etc.) less carbon atoms, and particularly easily in the case of certain substituted cycloalkanes.

SAMPLE-VACANCY (DIFFERENTIAL) CHROMATOGRAPHY

Similar studies on the hydrocracking reaction under hydrogen may be carried out using sample-vacancy (differential) chromatography and using a variation of flow-rate to give varying contact time. In this technique the reaction mixture (e.g. hydrogen and n-dodecane) is passed continuously through the reactor and a subsequent analytical gas chromatographic column to a detector. At intervals, samples of the unreacted mixture are then switched from before the reactor to after the reactor so as to generate a chromatogram leaving the analytical column in which positive (normal) chromatographic peaks measure the amount of reactant (n-dodecane) which has reacted in the reactor, while negative (vacancy) peaks the volatile products formed
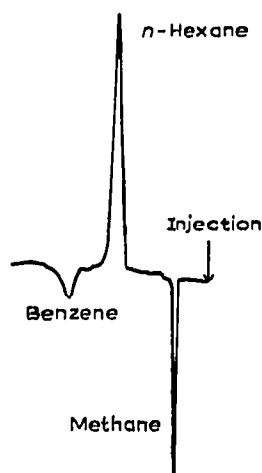

Fig. 4. Sample-vacancy chromatogram obtained during the hydrocracking of a stream of n-hexane on Ni-SiO₂ at 157° under nitrogen, and at a stage where the rate of reaction has become small.

in the reactor. The differences obtained from these two sets of peaks measure the amounts of non-volatile products (polymers, coke etc.) retained in the reactor. In general we have found this technique somewhat easier to use than that described in the previous section and it has been particularly useful in the study of the hydro-cracking of hydrocarbons under nitrogen rather than hydrogen carrier gas, where the formation of non-volatile products becomes more significant.

As an example, we may consider the reaction which occurs when a constant stream of *n*-hexane in nitrogen (1 part hexane to 5000 nitrogen) is passed through Ni–SiO$_2$ at 157° and then through an analytical column (10% squalane on Celite at 88°) to a flame ionisation detector. Under these conditions the only volatile reaction products are methane and some benzene in the later stages of the reaction. Fig. 4 illustrates a typical sample-vacancy chromatogram when the reaction rate has become fairly small. Fig. 5 gives the hydrocarbon composition of the gas leaving the reactor as a function of time in one particular experiment. In this case the nickel surface had been initially covered with hydrogen so that the hydrocracking reaction involved both this pre-adsorbed hydrogen and hydrogen from the hexane itself. When much of the hydrogen has been removed from the surface by heating at 350° for 7 h in a stream of nitrogen, the initial methane production is less and the hexane breaks through the reactor earlier.

It will be seen from Fig. 5 that the methane (stage 1 in Table II) production rate rises fairly rapidly to a plateau value from which it falls abruptly at the same time as the hexane breaks through. The plateau value is found to be quite independent of the pretreatment of the nickel surface with either hydrogen or nitrogen, but is naturally longer in the former case: this suggests that the reaction is essentially the same in both cases. Clearly the reaction occurs mainly in a zone of the reactor column (being built up until A and emerging from the column between the dotted line and B in Fig. 5) ahead of the hexane front and the plateau production of methane is controlled by
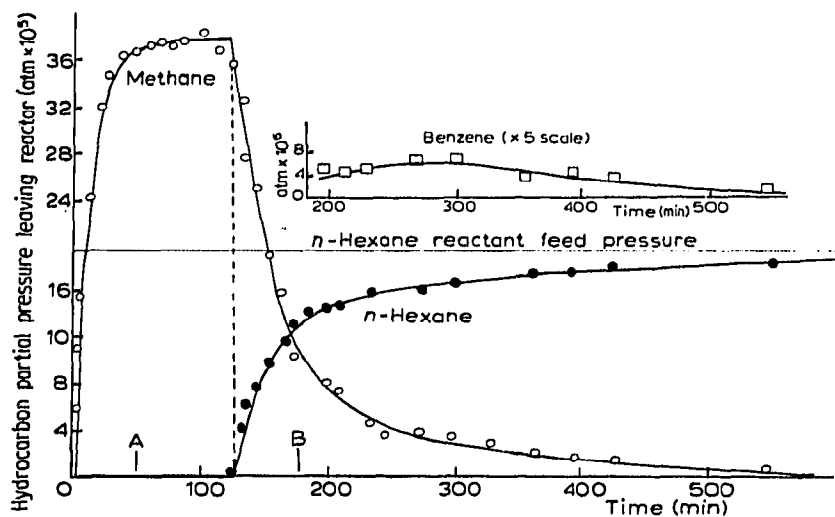

Fig. 5. The hydrocracking of an n-hexane stream on Ni–SiO$_2$ at 157° under nitrogen, as studied by sample-vacancy chromatography.

the rate of feed of hexane to the column. When the reaction has effectively ceased under nitrogen, the hexane–nitrogen feed is switched off and the column cleared with nitrogen. The carrier gas is then switched to hydrogen and a further quantity of methane (stage 2) is now produced. Some typical results for the numbers of carbon atoms involved in the stoichiometry are given in Table II.

TABLE II

EXAMPLES OF THE STOICHIOMETRY (IN TERMS OF C-ATOMS, MOLES $\times 10^5$) OF THE HYDROCRACKING REACTION OF n-HEXANE ON Ni-SiO₂ AT 157° UNDER NITROGEN

	Ni pretreated with hydrogen	Ni pretreated with nitrogen
Total hexane take-up by reactor	23.0	16.9
Methane (stage 1)	5.6	3.2
Benzene	0.9	0.7
Methane (stage 2)	12.7	11.6
C permanently retained	3.8	1.4

These experiments have been carried out so far under a reaction regime which differs markedly from that described in the previous section in that the hydrocarbon concentration has been somewhat lower (about 5 times) but probably most importantly because of the enormous change in the hydrogen pressure from 1 atm to virtually zero. The results differ in the following respects.

(i) The reaction takes place at a significantly lower temperature, suggesting that hydrogen acts as an inhibitor of the hydrocracking reaction[6].

(ii) No substantial amounts of C_5, C_4, C_3 or C_2 hydrocarbons are observed in the products. This presumably means that the C_5 fragment of the initial fission of n-hexane is not normally removed from the surface to give pentane before it has reacted further. However injection of hydrogen during the reaction under nitrogen immediately results in the production of a range of hydrocarbons from C_1–C_6.

(iii) Permanent loss of carbon to the reactor column is now significant as is shown in Table II, the loss in general being related to the methane produced in stage 1.

(iv) Benzene is formed in the latter stages of the reaction with yields of up to 10 % of the hexane: the quantity seems to be largely independent of the pretreatment of the nickel surface.

ACKNOWLEDGEMENTS

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