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GAS CHROMATOGRAPHY IN CATALYTIC STUDIES

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I. INTRODUCTION

The development of gas chromatography opens up wide possibilities in the study of catalytic processes. Gas chromatography makes it possible to obtain in a relatively short time information about the composition of the starting materials and products in catalytic processes, facilitates tests on catalysts, and greatly simplifies the experimental technique. A number of examples have been described of the successful use of gas chromatography in the analysis of the products of catalytic processes such as hydrogenation[1-5], dehydrogenation[6-8], isomerisation[9-12], dealkylation[13-15], oxidation of organic and inorganic substances[16-18], polymerisation[19-21], and reactions of organosulphur compounds derived from petroleum[22-24] and of other substances.

In many cases the method in which the catalytic reaction is performed in a flow microreactor attached directly to a chromatographic column proved very fruitful[25-29]. The use of labelled atoms in radiochromatography has been an effective means of studying the mechanism of catalytic processes[28,30,31].

Considerable interest attaches also to catalytic reactions under chromatographic conditions[30-33], whereby it is possible to obtain rapidly new, valuable data on the mechanism and the kinetics of the process and on the properties of the catalyst and their variation with time.

Finally, gas chromatography is a rapid method for the determination of the isotherms and heats of adsorption, the specific surfaces of catalysts, and their surface structure, acidity, and catalytic activity[34-39].

II. QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE PRODUCTS OF CATALYTIC PROCESSES

The study of the majority of catalytic processes is impossible without qualitative and quantitative analysis of the initial materials and the reaction products. In these studies gas chromatography often proves to be the most effective analytical method both in laboratory tests and in the control of industrial processes[40-44].

The methods of analysis of the products of catalytic processes must as a rule meet very stringent requirements, particularly if the reactions are fast and rapid analysis is necessary. For this reason, the shortening of the duration of analysis while maintaining adequate capacity for separation and adequate precision is one of the principal requirements which must be satisfied by a gas-chromatographic method. In many catalytic processes very complex mixtures of substances of different types are obtained, the concentrations of the individual components varying between very wide limits[6,40,41,45]. It is very difficult to separate such mixtures and to analyse them qualitatively and quantitatively.

On the other hand, the determination of trace impurities in the starting materials or the catalytic reaction products is no less complex a problem[46]. The total analysis of the products is frequently interfered with by the presence in the latter of unstable or reactive compounds, substances tending to polymerise, and also water[16,47-49]. It is therefore often necessary to perform extensive preliminary experiments in order to find the most favourable conditions for the chromatography of such mixtures.

Qualitative analysis. Qualitative analysis in gas chromatography is usually concerned in the first place with

the determination of the retention time (or volume)[50-54]. Several methods are known for the identification of chromatographic peaks, based on the measurement of these quantities: (1) determination of the relative retention volumes of the substances being analysed and the pure compounds, in relation to some standard, on several liquid phases; (2) the use of the variation of the logarithm of the retention volume of the given substance with the number of carbon atoms, which is linear within a homologous series; (3) determination of the relation between the logarithm of the retention volume and the factor $Z = T_b/T$, where T_b is the boiling point of the substance and T the column temperature; (4) the use of retention indices (the Kováts method).

Until recently the first method was most frequently employed. A large number of tables and individual data on the relative retention volumes of substances of a wide variety of classes of various liquid phases and adsorbents have been published[50-54]. However, the use of these data is difficult because different workers have used different substances as standards and have made measurements at different temperatures, as a result of which the data are often inconsistent[55].

More reliable results are provided by plots of the logarithms of the retention volumes against the number of carbon atoms or against the boiling points of substances within a single homologous series at a given column temperature. Extensive experimental data on the identification of the homologues of various classes of organic compounds on eighteen liquid phases have been presented by Tenney in the form of such graphs[56].

Zhukhovitskii and Turkel'taub[53] proposed to use the relation between the logarithm of the retention volume of a given substance and the factor Z, defined as the ratio of the boiling point of the substance and the column temperature. For members of a single homologous series, this relation is approximately linear. The identification reduces to finding the boiling point of the test substance from the plot and comparing it with tabulated data. An advantage of this method of identification is that it permits measurements at different temperatures, which is inevitable when the mixture contains components with sharply different boiling points.

Recently the retention indices proposed by Kováts[57-61] have been receiving an increasing amount of recognition. This method of qualitative identification is based on the use of the familiar relation between the logarithms of the retention volumes and the number of carbon atoms in straight-chain paraffins, the logarithms of the retention volumes of such straight-chain paraffins being adopted as an index I scale. In this scale the retention indices for straight-chain hydrocarbons are assumed to be equal to the number of carbon atoms multiplied by one hundred and the indices of other substances, which have intermediate values, are found from the formula

$$I = 100\frac{\ln V_R - \ln V_{R(n\text{-}C_n)}}{\ln V_{R(n\text{-}C_{n+1})} - \ln V_{R(n\text{-}C_n)}} + 100n,$$

where V_R is the true retention volume of the test substance (i.e. the retention volume corrected for the dead space in the column), $V_{R(n\text{-}C_n)}$ the true retention volume of a straight-chain paraffin with n carbon atoms, and $V_{R(n\text{-}C_{n+1})}$ the true retention volume of a straight-chain paraffin with $n + 1$ carbon atoms; we have

$$V_{R(n\text{-}C_n)} \leqslant V_R \leqslant V_{R(n\text{-}C_{n+1})}.$$

The method of expressing the retention volumes in the form of indices has a number of advantages, the most important of which are as follows.

1. The standard is not a substance selected at random but the homologous series of straight-chain hydrocarbons, which enhances the precision of the determination of the indices, and the latter can be reproduced in other laboratories with greater reliability.

2. The difference between the retention indices for a single substance on two liquid phases, polar and non-polar, characterises its chemical nature, which facilitates the qualitative analysis. At the same time, this difference can serve as a quantitative characteristic of the polarity of the chosen liquid phase.

3. When literature data on the retention indices are available, qualitative analysis without pure substances is possible, which is of considerable interest in the analysis of multicomponent mixtures of unknown composition[61].

4. The Kováts indices vary with temperature much less than the simple relative retention volumes, which facilitates the use of literature data obtained at different temperatures[62].

The system of Kováts indices is probably the most universal and the most promising, as evidenced by the fact that an increasing number of investigators have used them in their studies. At the present time tables of retention indices are being compiled for substances of different classes on a wide variety of liquid phases[58,60,63]. In the determination of the retention indices it is essential to exclude as far as possible the effect of adsorption on the solid support, which is particularly pronounced in the chromatography of polar substances[64,65]. In this connection the work carried out to find new supports and to improve the properties of the commonly used inert supports merits attention[66-84]. The technique of liquid phase deposition also has an important role[85].

In the study of new catalytic processes, whose products consist of complex mixtures of unknown composition, it is desirable to check the results of identification based on the retention time or volume by another independent method. Infrared spectroscopy and mass-spectroscopy have found very wide application recently in the analysis of fractions emerging from gas-chromatographic columns[1,86-99]. The combination of gas chromatography with nuclear magnetic resonance is of considerable interest. For example, using this combination of methods, it proved possible to identify the products of complex catalytic processes, such as the condensation of isobutene with formaldehyde[45] and others[100,101]. Examples of the application of polarography in the analysis of fractions eluted from the chromatograph have also been described[102].

In the analysis of complex mixtures preparative gas chromatography, in which considerable advances have now been made[103-107], may prove very useful. Frequently in the identification of chromatographic peaks use is made of chemical reactions specific to pure substances or classes of substances, which are carried out either with the initial mixture to extract or convert a number of products or with fractions collected at the outlet from the chromatograph[108-112]. A method of carrying out such reactions directly in the injector containing the test sample in the vaporised state has been described[109,110].

Chemical reactions can also be conveniently performed in a reactor connected to the chromatograph and the carrier

gas source. The reactor is filled with a suitable reagent or catalyst and maintained at a specified temperature, the reactants being introduced with the carrier gas. For example, in the qualitative analysis of substances of different classes the latter may be catalytically hydrogenated to the corresponding hydrocarbons, which are more readily identified [113-116].

Dravert and other investigators [117-121] extended the range of reactions which can be carried out in a microreactor – they converted the starting material into ethers, saturated and unsaturated hydrocarbons, etc. They showed that this method (which they called reaction chromatography) is not only a means of qualitative analysis but can also be used for quantitative determinations. In many cases it leads to a simplification of the chromatographic process, particularly if the mixture to be analysed contains high-boiling polar substances (for example, alcohols, glycols, acids, hydroperoxides, etc.) [122,123].

A number of workers [124-126] have used pyrolysis with subsequent chromatographic analysis of its products for the qualitative identification of the components of complex mixtures and the analysis of complex organic substances and polymers. The resulting chromatograms are compared with the chromatograms of the pyrolysis products of the substances which are expected to be present. The chromatogram of the pyrolysis products of a compound constitutes a characteristic spectrum, resembling the mass spectrum. The ratios of the peak intensities (heights) may serve as a qualitative characteristic of a given substance.

The literature on reaction chromatography, including pyrolysis, has been reviewed by Berezkin and Gorshunov [127].

Quantitative analysis. Quantitative analysis in gas chromatography is based on the calculation of chromatograms. There are several methods of calculation, depending on the parameters of chromatographic peaks used [53,128]. In practice, the peak area is normally employed as the parameter in the calculation. A number of methods have been described for the determination of peak areas [53,129-134]. In order to obtain accurate quantitative results, it is important to choose the most suitable method for each particular case, depending on the magnitude and shape of the chromatographic peaks. It should also be noted that the use of integrators greatly facilitates the measurements and yields accurate results when all the peaks in the chromatogram are fully separated, regardless of their shape [135-137]. When the separation is incomplete, quantitative analysis based on a detailed study of the shape of the peaks and the mode of their superposition is possible. Several methods for the calculation of incompletely resolved peaks have been described [134,138].

The ratio of peak areas is usually not the same as the ratio of the concentrations of the mixture components. In the first place, this is due to the different sensitivities of the detector to different substances and in the second place to the non-linearity of the detector response. The effect of these factors on the results of quantitative analysis can be taken into account by means of calibration against pure substances and artificial mixtures. Usually three methods of calibration are employed: the method of absolute calibration, the method of internal normalisation (taking into account the coefficients of the sensitivity of the detector to different components), and the internal standard method. The applicability of a particular method depends on the qualitative composition of the mixture to be analysed, on the concentration ratios of its components, on the properties of the detector (the range of linearity, sensitivity, etc.), and certain other factors. This problem has been adequately treated in monographs on gas chromatography [53,54,128] and in the recently published review of Andreev et al. [134], where molar correction coefficients for substances of different classes and detectors of different types have been tabulated.

In the analysis of the products of catalytic processes, both under laboratory and industrial conditions, the problem of the choice of the correct method of sample injection into the chromatograph frequently arises, since it determines the quality of the separation and the reproducibility of the quantitative results [53,139]. At the present time gaseous samples with accurately specified volumes can be most readily introduced by means of dosimetric taps of different designs [128,140-142]. For this reason, an attempt is often made to meter out the liquid samples in the vapour phase. The problem then reduces to the design of sampling taps which would remain gas-tight at an elevated temperature (to prevent the condensation of the mixture components) and which would ensure the required reproducibility of the metering [142-144]. When such taps are present, vaporised mixtures of products of catalytic processes can be analysed directly at the outlet of the reactor without preliminary condensation and trapping, which greatly shortens the duration of the analysis and simplifies the experimental method.

Liquid and solid samples are usually introduced by means of microsyringes, micropipettes, sealed tube breaking devices, and certain other procedures [54,145-147]. All these methods have a number of disadvantages which must be taken into account in the experiments to reduce their effects. Among all the devices, microsyringes are preferred [148]. Reactive substances are introduced in sealed tubes [145].

Let us now consider briefly the methods of accelerating gas-chromatographic analysis, since frequently the duration of the study of a catalytic process is determined by the rate of analysis of its products. The problem of the acceleration of chromatographic separation is indissolubly linked to the efficiency of the column, the selectivity of the liquid phase or the adsorbent, and also the retention time. In many cases involving a high degree of separation the duration of analysis may be shortened by decreasing the proportion of liquid phase, by increasing the temperature of the column and the flow rate of the carrier gas, and by using as the latter hydrogen or helium which have low viscosities [149,150].

The separation of multicomponent mixtures over a wide range of boiling points of the components is greatly improved if the column temperature is increased during the analysis, which is achieved by temperature programming [151-153] and by a chromathermographic technique [53,154,155]. To shorten the duration of analysis, it is convenient to use surface-porous adsorbents and carriers, with pores only at the surface itself, for example porous glasses [156], glass microbeads which have been etched or covered by a layer of a highly dispersed substance [75,157], and other materials. The analysis can be greatly accelerated by decreasing the column diameter [158] and by employing capillary chromatography [53].

Apart from reducing the time of separation, chromatography at reduced pressures provides more favourable separation conditions. It is then possible to reduce considerably the column temperature (since the volatility of the components increases), which enhances the selectivity of the liquid phase and analysis of thermally unstable substances becomes possible [159-161]. Reaction gas chromatography may be used for

the same purpose, whereby high-boiling polar substances can be converted into readily volatile compounds [117-119].

A number of workers have attempted [162,163] to calculate theoretically the minimum time for analysis in capillary and packed columns. Examples of the separation of multicomponent mixtures during the periods of the order of one minute have been given. The chromatograms are recorded with the aid of an oscilloscope [150].

III. CATALYTIC PROCESSES IN A MICROREACTOR (RADIOCHROMATOGRAPHY). THE STUDY OF CATALYTIC REACTIONS UNDER CHROMATOGRAPHIC CONDITIONS

The advantages of the gas-chromatographic method of analysis are most fully shown in the study of catalytic processes in a microreactor attached directly to the separating column of the chromatograph. Either inert gases or gaseous starting materials (H_2, O_2, and others) are used as the carrier gas. The remaining starting materials are introduced into the reactor periodically and are transferred by the carrier gas through a layer of catalyst into the chromatographic column, where the products and the unreacted components of the initial mixture are separated. By carrying out the process in a microreactor, it is possible to investigate over a short period the activity and selectivity of a large number of catalysts while varying various parameters (temperature, space velocity, pressure, etc.) [28,29,164-166].

Catalytic processes in a microreactor are as a rule fast and analysis of the products is the rate-limiting stage in the investigation of reactions and catalysts. For this reason, gas chromatography, which is one of the fastest analytical methods, is the most convenient in this case. In the study of catalytic processes in a microreactor, it is essential to exclude possible analytical errors due to, for example, the sorption of substances on the catalyst, the non-identity of the conditions obtaining in the calibration and in the analysis, the inadequacies in sample injection, etc. It is essential to achieve satisfactory reproducibility of the quantitative chromatographic analysis, since in each experiment it is possible to obtain only one chromatogram. At the present time the system comprising a chromatograph with a microreactor is widely used in the study of both the catalysts themselves [167] and various catalytic processes: hydrogenation and dehydrogenation [25,26], oxidation [27,168], cracking [28], polymerisation [19], and others.

In the study of the molecular mechanism of reactions, tracer atoms and radiochromatography may prove very useful. The essential feature of radiochromatography is the addition to the initial mixture of one of the components which is radioactively labelled. The products of the catalytic reaction are separated and analysed in a chromatograph with two detectors connected in series, for example a katharometer and a radiometric cell. Comparison of the chromatograms obtained with the aid of the two detectors shows which products can be obtained from the substance labelled with a radioactive isotope [28,169]. If a labelled substance, which according to the postulated possible mechanisms of the process is an intermediate, is added to the starting materials, then, by measuring the specific activity of the final products, it is possible to investigate the mechanism and kinetics of the individual stages of the reaction (Neiman's method) [170-172]. Such investigations are usually performed using a microcatalytic apparatus, since the study of the process in a microreactor requires only small amounts of the starting materials. Of course, the results obtained in a microreactor cannot describe the process as a whole. The selectivity of the catalyst may change on going to larger apparatus. It is also possible that under conditions obtaining in the microreactor optimum operation of the catalyst is not always achieved and therefore caution must be exercised in approaching the problem of catalyst selection on the basis of such data alone. However, microcatalytic apparatus with chromatographs can be used successfully in the study of the mechanism of catalytic processes.

Catalytic reactions under chromatographic conditions are more specific. This method is used in the study of both various types of reaction and of the changes in the catalysts during the experiments (exploitation, poisoning, and regeneration) [30-33,173,174]. A microreactor with a catalyst is also used in catalytic reactions under chromatographic conditions. The starting material is introduced as a separate sample (pulse) into the reactor and is transferred by the inert carrier gas or by a gaseous reactant to a layer of catalyst. The reaction products and the starting materials are separated on the catalyst itself and are analysed at the outlet from the reactor by means of a suitable detector.

The conditions of catalytic reactions in pulse chromatography differ from those usually encountered. Thus under chromatographic conditions the intermediate and final products are separated from the starting materials and therefore the interactions between them and the reverse reactions are almost completely excluded. The conversion then increases sharply. In those cases where any one product is not separated from the starting material on the catalyst, it is possible to investigate the process with the latter inhibited by its products and to assess the effect of such inhibition.

Furthermore, under chromatographic conditions the reactants are freed from impurities (except for the impurities present in the carrier gas), which may be catalyst poisons, inhibitors, promoting agents, or initiators. The effect of these impurities can also be investigated [173].

The characteristic features of the chromatographic conditions make it impossible to use this method to investigate the reactions of two or more starting materials in an inert carrier gas, since, as a result of the chromatographic separation of the initial mixture, the reactant molecules do not meet either in the gas phase or on the catalyst surface.

The chromatographic conditions can be conveniently used for reactions of the type

$$A \rightleftarrows B + C,$$

which are fairly fast but have low equilibrium constants [32]. However, an example of reactions of the type

$$A + B \rightarrow C + D.$$

under chromatographic conditions has been described [175]. One of the starting materials is then either continuously passed through the catalyst in the stream of the carrier gas or introduced as a pulse, mixed with other components. Probably in this case the starting materials are not separated in the reactor and therefore reaction between them is possible.

Roginskii and coworkers made a theoretical analysis of heterogeneous catalytic reactions of various orders under conditions of ideal linear chromatography and derived

equations for the rate constants and the activation energies for first-order reactions, which they used in the study of the dehydrogenation of cyclohexane to benzene on a number of catalysts [33]. They showed [176] that the rate constants for the reaction can be determined not only from the degree of conversion at various carrier gas flow rates but also from the shape of the product output curve obtained at a single carrier gas flow rate, on the assumption that under the experimental conditions the adsorption isotherm of the product on the catalyst is linear.

The use of radioisotopes and of an additional radiometric detector provides in this case too an effective means of determining the mechanism of the process when the latter is carried out under chromatographic conditions. For example, confirmation has been obtained of the absence of the reverse reaction in the dehydrogenation of cyclohexane on a platinum catalyst in an inert carrier gas [31] and in the dehydrogenation of butenes to divinyl under chromatographic conditions [177].

The results of the study of a catalytic process under chromatographic conditions provide additional information both about the process itself and about the state of the catalyst. The possible advantages of these conditions in industry have not so far been considered. The possibility that in some processes pulse conditions may prove effective cannot be excluded.

IV. GAS-CHROMATOGRAPHIC STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF CATALYSTS

In heterogeneous catalysis chemical processes are accompanied by adsorption. Therefore the study of the adsorption properties of catalysts constitutes a very important problem. The main characteristics of adsorbents are their structural properties (specific surface, porosity, i.e. quantities which are independent of the properties of the substances adsorbed) and their properties determined by the nature of the adsorbent–adsorbate system (adsorption energy, adsorption isotherm, and others).

Since in gas chromatography the retention time (volume) and the shape of the peak due to a given substance depend on the properties of the adsorbent and the substance adsorbed, it was natural to consider the reverse problem: to investigate on the basis of chromatographic data the properties of adsorbents and catalysts with the aim of reducing the time required for chromatographic investigations. It was found that, with certain assumptions, it is possible to establish a mathematical relation between the specific retention volume of a given substance and the specific surface of the catalyst [36] and between the shape of the chromatographic peak and the adsorption isotherm [178], while the temperature variation of the retention volume makes it possible to determine the heat of adsorption [39]. A chromatographic method for the determination of the activity of certain catalysts has also been described [37].

In most of the studies dealing with the determination of the surface area of adsorbents and catalysts by gas chromatography, use is made of the relation, derived by Wilson, between the form of the chromatographic curve and the form of the adsorption isotherm in the absence of complications associated with the kinetics of the adsorption and longitudinal diffusion (conditions of equilibrium chromatography) [35,179-181]. On the basis of chromatographic data, it is possible to obtain adsorption isotherms on catalysts at different temperatures and to determine the absolute specific surface of the catalyst. Either adsorption–desorption curves or display chromatograms are then employed.

However, more accurate results are given by Nelsen and Eggertsen's thermal desorption method [34,182,183], in which the conditions of equilibrium chromatography are not required, this being particularly important in the study of finely porous adsorbents and catalysts. This method constitutes the basis of gas-chromatographic sorption meters [184,185].

By using as adsorbates substances of different molecular size, it is possible to estimate the nature and distribution of the pores with respect to radius [186]. A method has also been described for the determination of the relative surface area, based on the determination of the specific retention volume V_g at low concentrations, which is proportional (within the limits of experimental error) to the specific surface S_g: [36,187-189]

$$S_g = AV_g \qquad (1)$$

where A is a proportionality coefficient, which depends on the nature of the adsorbent–adsorbate system and on temperature. Eqn. (1) has been tested on a large number of catalysts [36]. The method is recommended for the measurement of the variation of the catalyst surface during its operation and also for rapid estimates of the surface areas of adsorbents and catalysts of the same chemical type.

Kiselev and coworkers [190,191] suggested that the retention volume of a given substance, referred to unit area of the adsorbent, be used as a characteristic of adsorbent–adsorbate systems:

$$V_s = \frac{V_g}{S_g},$$

where V_s is independent of the adsorbent surface area and reflects mainly the properties per unit surface.

The gas-chromatographic method can also be used to investigate chemisorption. Adsorption isotherms and isochores have been obtained for hydrogen on a number of metals and the kinetics of its chemisorption have been studied [192]. Such data may be useful in the investigation of hydrogenation catalysts.

The gas-chromatographic method has also proved an effective means for the investigation of catalysts with acid properties. Thus the total number of acid centres and the strength of their acidity under conditions obtaining in the operation of the catalyst can be found from the amount of chemisorbed ammonia (or an organic base), which can be readily obtained from a frontal chromatogram [183,193]. The effect of surface acidity on the adsorption of hydrocarbons and on catalyst activity has also been investigated with the aid of gas chromatography [38,193,194].

Misono et al. [38] proposed a gas-chromatographic method for the simultaneous determination of the distribution of acid centres with respect to the strength of their acidity and catalytic activity under conditions obtaining in the operation of the catalyst. The method consists in the determination of the retention volume and the heat of adsorption of benzene (a weak base) on the catalyst at different surface coverages of the latter with pyridine (a strong base). From these data, it is possible to construct the curve representing the distribution of the acid regions with respect to the strength of their acidity in terms of the benzene heat of adsorption scale, assuming that pyridine blocks such regions, starting with the most acid ones. If instead of benzene a reactant is admitted to the catalyst, it is possible to investigate, on the basis of the reaction products corresponding to different degrees of poisoning of the acid

centres by pyridine, the activity and selectivity of the catalyst in relation to different types of reaction, depending on the acid strength.

The results obtained in the study of the distribution of acid centres with respect to their acid strength obtained by the above method have been confirmed qualitatively by an indicator method. The advantage of the chromatographic technique is that the determination of the acidity is performed under the conditions of the catalytic process itself. Furthermore, the colour of the catalysts, which interferes with indicator measurements, is without importance in the chromatographic method.

The application of gas chromatography in the determination of the heat of adsorption is based on the fact that, under conditions of ideal chromatography (when the isotherm is linear), the logarithm of the retention volume of the given substance is proportional (after certain necessary corrections) to the free energy of adsorption, and the heat of adsorption can be found from the slope of the linear plot of the logarithm of the adsorbate retention volume against the reciprocal of absolute temperature[39,195,199]. It is assumed that the effect of diffusion and of the finite rate of mass exchange is slight and may be neglected[199]. A chromatograph designed specially for the measurement of heats of adsorption has been described[200]. While it cannot replace the more reliable and detailed calorimetric technique, the chromatographic method permits rapid, simple, and fairly accurate determination of the heat of adsorption.

Comparison of the heats of adsorption determined by both methods shows good agreement in most cases. The discrepancy between the results is mainly due to the different surface coverages used in the two methods[39,198]. Since gas chromatography is highly sensitive, it permits the determination of the heat of adsorption at surface coverages so low that there is no interaction between the adsorbed molecules even when they are capable of association. On combining this method with some other, applicable to higher coverages (for example the calorimetric method), it is possible to determine the energy of association in the adsorption layer. The energy of the hydrogen bond between molecules of alcohols adsorbed on the surface of graphitised carbon blacks has been determined in this way[201,202].

The chromatographic method makes it possible to extend the range susceptible to investigation to temperatures of 300–500° and to measure the heat of adsorption under conditions close to those in a catalytic reaction. These advantages are lacking in the calorimetric method and in the method involving the calculation of isosteric heats from adsorption data, which are usually employed[197,199]

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