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Reactions on Catalyst Surfaces under Programmed-heating Conditions

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The temperature-programmed reaction method and the principles of the calculation of the kinetic parameters of the surface stages of a catalytic process have been described. The influence of surface non-uniformity and the limiting stage on the parameters obtained has been examined. The possibility of detecting intermediate products of surface reactions has been analysed.
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I. INTRODUCTION

The large number of studies of catalytic processes, including the stages of adsorption, the surface reaction, and desorption, indicate the complexity of the reactions of gases with solid surfaces. Even when catalysts with well characterised surfaces, for example metal single crystals, are used, the interpretation of the data obtained under stationary reaction conditions is extremely difficult. It is therefore natural to study the kinetics and mechanism of these processes by non-stationary methods, in particular the familiar thermal desorption (TD) method, which has been widely used to study the energy parameters of the reaction of simple gases with pure metal surfaces.[1,2] One of the first studies of the use of this method in catalysis was carried out in the 1960's,[3] and since then the number of studies carried out by the TD method has increased continuously.[4-6] The present review examined chiefly work carried out in the 1970's and 1980's, and deals with the problems of the reactions of gases with surfaces of interest for catalysis.

II. PRINCIPLES OF THE METHOD AND THE CALCULATIONS

1. The Temperature-programmed Reaction Method

The temperature-programmed reaction (TPR) or temperature-programmed surface reaction (TPSR) method involves the adsorption of the substance being studied on a catalyst surface under given conditions, the removal of molecules of the original substance from the gas phase, and subsequent heating of the catalyst (usually at a constant rate) with simultaneous analysis of the products liberated at definite time intervals or at different catalyst temperatures. TPSR differs from thermal desorption in that in the first case the adsorbed substances undergo various transformations on the catalyst, that is a surface reaction takes place and the products of the transformation are liberated into the gas phase, whereas in the second case the adsorbed and desorbed species have the same composition. The main experimental approaches can be divided into two groups, depending on the methods used to remove and analyse the products from the gas phase: the chromatographic version,[3] in which the removal of the reaction products and the chromatographic analysis are carried out using an inert carrier gas, and the vacuum version, which originates from the first studies of the thermal desorption of simple gases from metal surfaces,[1,2] and which involves the vacuum treatment of the specimen after adsorption and mass-spectrometric analysis of the desorbed products. In the last case, the experiments can be carried out in closed systems or in flow systems.

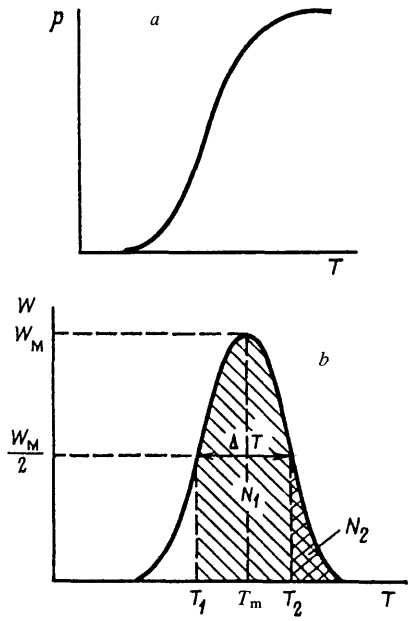


Figure 1. Schematic representation of the desorption curves in closed (*a*) and flow (*b*) systems. The hatched areas correspond to the concentrations of the molecules on the surface at temperatures T_1 and T_2; T_m is the temperature of the peak maximum.

Fig. 1*a* gives a schematic representation of the temperature dependence of the pressure of the desorbed substances (p) in a closed system. Differentiation of the curve in Fig. 1*a* makes it possible to find the dependence of the rate of liberation of the product into the gas phase on time (that is the catalyst temperature). The same dependence (of W on T)

can be obtained by carrying out TD and TPSR in a flow system (Fig. 1*b*) at sufficiently high rates of evacuation. Although carrying out the experiments in a flow system lowers the sensitivity of the method, it makes it possible to avoid graphical differentiation, that is to increase the accuracy of the determination of the kinetic parameters; moreover, as a consequence of the decrease in the pressure in the system, it is possible to neglect the re-adsorption of the desorbed gases. For a flow system, the equation for the material balance of the product liberated in the gas phase can be written as follows:

$$V\frac{dp}{dt} = W - ps \qquad (1)$$

where V is the reactor volume, W the rate of desorption, p the pressure of the given component of the gas mixture, and s the rate of evaucation. Each term of Eqn.(1) is usually expressed in litre.mmHg s^{-1}, from which values of the rate of desorption expressed in molecule s^{-1} can readily be obtained. If $V(dp/dt) \ll ps$, it follows that

$$W = ps \qquad (2)$$

In the chromatographic version of TD and TPSR, the material-balance equation in the absence of re-adsorption has the form:

$$W = Fc \qquad (3)$$

where F is the velocity of the stream of carrier gas, and c the concentration of the desorbed substance in the carrier gas. Eqns.(2) and (3) have similar forms, and make it possible, by measuring the pressure of the gas above the specimen or the concentration of the desorbed substance in the carrier-gas stream during the TPSR, to determine directly the time (temperature) dependence of the rate of removal of substance from catalyst surfaces into the gas phase.

A term describing the rate of re-adsorption is often included in Eqns.(2) and (3). In a number of cases, allowance for the rate of re-adsorption is necessary,[7] but this complicates the kinetic equations considerably and makes it necessary to study the adsorption separately, so that it is practically impossible to analyse the equations obtained. It is therefore usually preferred to create experimental conditions under which re-adsorption can be neglected, and the rate of desorption can be determined from Eqns.(2) and (3). A sufficiently correct analysis of the influence of re-adsorption on the form of the TD curves has been published.[3,5,8]

As already noted, the products can be analysed chromatographically or mass-spectrometrically. In the first case the desorption products are directed together with the stream of carrier gas into a thermal-conductivity or flame-ionisation detector, and the time (temperature) dependence of the concentration of the product is recorded, that is the TD peak is obtained directly. This method is simple and sufficiently reliable if only one reaction product is liberated. Otherwise, the chromatographic analysis of each substance is necessary, and a series of several peaks, or, as it is usually described, a TPSR spectrum, is obtained. When peaks overlap (when different substances are liberated simultaneously), the problem is complicated, and it is very difficult to obtain TD peaks for each substance separately, even by successive sampling of the products, for example by freezing before chromatographic analysis.

Continuous mass-spectrometric analysis of the gas phase makes it possible to avoid these difficulties, since the change in the concentration of each substance can be followed. The mass spectrometers used for this purpose must satisfy a number of requirements, however. Firstly, the range of masses recorded should cover all the substances studied, including that with the highest molecular mass. It is also necessary to be able to vary the ionising voltage, in order, for example, to reduce as far as possible the extent of the fragmentation of the molecules in the mass spectrometer and hence facilitate the interpretation of the mass spectra obtained. Secondly, the time taken to record the entire mass spectrum should be so short (usually 0.1–1 s) that it is possible to obtain the complete spectrum at the same catalyst temperature. Experience has shown that these requirements are most fully satisfied by quadrupole, monopolar, and time-of-flight mass spectrometers (of the instruments produced in the USSR, the MKh-7304 and MSKh mass spectrometers). It is particularly convenient to use mass spectrometers in which it is possible to record continuously several fixed masses in the computer memory, so that the TD curves for each substance can subsequently be constructed separately.

No special requirements have to be satisfied by the reaction cell in which the catalyst specimen is placed. It is necessary only to note that the volume of the cell should be such that the quantity of catalyst, on the one hand, corresponds to the sensitivity of the recording system, and on the other hand is the minimum quantity, to avoid re-adsorption. The temperature of the specimen is usually measured by a thermocouple placed in the layer of catalyst. It is first necessary to be sure that there are no radial and axial temperature gradients; at the heating rates usually employed (b = 0.01–1 K s^{-1}), these effects are insignificant.

2. Methods for Determining the Kinetic Parameters of TD and TPSR

One of the problems in TD and TPSR is the determination of the kinetic parameters of the processes of desorption and the surface reaction respectively. In spite of the variety of methods for determining these parameters, they are all based on the Polanyi–Wigner equation

$$W = -dN/dt = kN^n \exp(-E/RT) \qquad (4)$$

where W is the rate of desorption (or of the surface reaction accompanying desorption), k the pre-exponential factor, N the concentration of adsorbed substance, n the kinetic order of the process, E the activation energy, and T the temperature of the catalyst surface.

One method for determining k and E is the so-called linearisation of the thermal desorption curve. In this case, Eqn.(4) and the experimental data (see Fig. 1*b*) are used to construct the plot of $\ln(W/N)$ against $1/T$ or of $\ln(W/N^2)$ against $1/T$ (for processes of first or second order respectively). The concentration (N) of the substance remaining on the surface at each temperature is determined as the fraction of the area under the TD curve bounded on the left-hand side by the corresponding temperature (as an example, Fig. 1*b* gives N_1 and N_2 for temperatures T_1 and T_2). The slope of the straight line on Arrhenius coordinates gives the activation energy of the process. For this it is sufficient to know the relative values of the rates of liberation of the substance into the gas phase and the degrees of covering (N). To determine the pre-exponential factors by this method, however, it is necessary to have data on the absolute values of the rates.

Since in TD and TPSR experiments both the temperature and the degree of covering change continuously, the usual methods for determining the order of the reaction, for example from the dependence of the rate of the process on concentration (in this case the degree of covering) are not applicable, and the order is found from the best agreement

with experimental data from the $\ln(W/N)-1/T$ or $\ln(W/N^2)-1/T$ plots.

If the catalyst is heated by a linear programme ($T = a + bt$) and account is taken of the fact that at the maximum of the TD peak at T_m (see Fig.1*b*) $dW/dT = 0$, then Eqn.(4) gives:

$$E/RT_m = \ln\frac{knN^{n-1}T_m}{b} - \ln(E/RT_m) \qquad (5)$$

or, in slightly modified form, for a process taking place, for example, according to first order kinetics:

$$2\ln T_m - \ln b = E/RT_m + \ln(E/kR) \qquad (6)$$

Eqn.(6) was first proposed by Amenomiya and Cvetanovic.[3] It can be seen from Eqns.(5) and (6) that T_m for the TPSR peak depends on the heating rate. If the dependence of $(2\ln T_m - \ln b)$ on $1/T_m$ is determined experimentally, Eqn.(6) can be used to find the parameters k and E being sought. This method has been called the "displacement of the temperature of the maximum with change in the heating rate" method or the method of Amenomiya and Cvetanovic. Here it should be noted that the experiments must be carried out at constant original degrees of covering of the surface, since otherwise T_m may change even for a constant heating rate. Thus Eqn.(5) and Fig.2 show that it is only for a first-order process that T_m is independent of the degree of covering of the surface, and that for a second-order reaction, T_m decreases, and for a zeroth-order reaction T_m increases, with increase in the original concentration of the adsorbate. For second-order processes, the form of the TD peak is symmetrical.

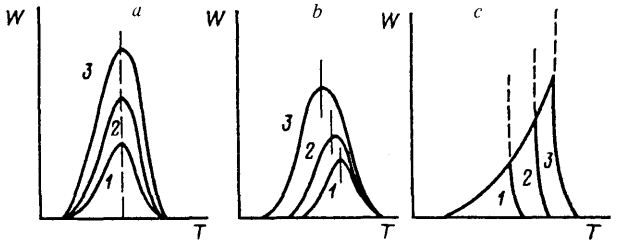


Figure 2. Schematic representation of the TD curves for processes of first (*a*), second (*b*), and zeroth (*c*) orders; the original coverage increases from (*1*) to (*3*).

To determine the kinetic parameters of desorption and surface reactions, extensive use has been made of a method based on the measurement of the so-called half-width of the TD peak $\Delta T = T_2 - T_1$, that is the difference between the temperatures at which the rate of the process is equal to half the maximum rate (see Fig.1*b*).[9,10] According to Eqn. (4), the expressions for the rates of the process at T_1 and T_2 can be written in the form:

$$\frac{W_m}{2} = kN_1^n\exp(-E/RT_1); \quad \frac{W_m}{2} = kN_2^n\exp(-E/RT_2) \qquad (7)$$

which gives:

$$E = \frac{R\ln(N_1/N_2)^n T_1T_2}{\Delta T}. \qquad (8)$$

Eqn.(8) shows that the factor $T_1T_2/\Delta T$ is independent of the heating rate. It is therefore possible to determine the activation energy from one experiment. Computer calculations by the present author showed that the first-order processes, $\ln(N_1/N_2)$ is constant, and that for second-order processes, $\ln(N_1/N_2)^2$ changes little, even with change in the concentration by a factor of 10. Using the calculated values of these parameters, the expressions for the activation energies of the first- and second-order processes can be written in the form:

$$E = 4.6T_1T_2/\Delta T \text{ for } n = 1;\ E = 6.2T_1T_2/\Delta T \text{ for } n = 2. \qquad (9)$$

The order of the reaction can be estimated from the form of the peak (see Fig.2). A more accurate equation for calculating E for second-order processes using the half-widths of the TD peaks has been proposed.[11] The pre-exponential factors can be calculated (if the value of E is known) using Eqns.(4) and (5) or a simplified form of Eqn.(5).[9]

The method in which E is determined using the parameter ΔT and hence Eqn.(9) or the published equations[11] is much less sensitive to various experimental errors than the method based on the measurement of the dependence of T_m on the heating rate.

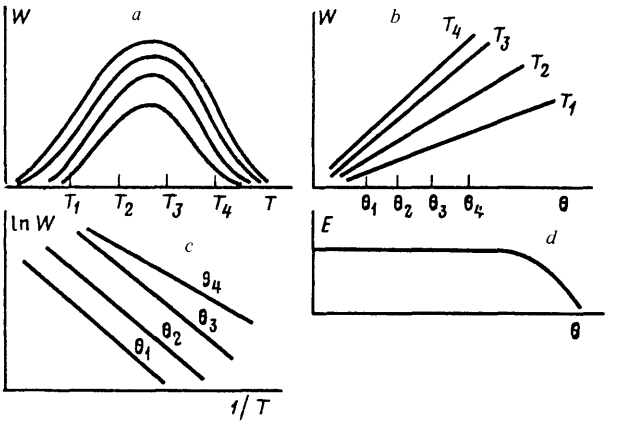


Figure 3. The method of "desorption isotherms": *a*) family of desorption curves for different original degrees of covering, *b*) desorption isotherms, *c*) Arrhenius relationships for constant degrees of covering, *d*) dependence of E on the degree of covering.

The above methods for determining the kinetic parameters are applicable to the analysis of individual TD or TPSR peaks reflecting processes taking place on uniform surfaces. For the analysis of processes taking place on non-uniform surfaces, the so-called method of "desorption isotherms" has been proposed.[12,13] It is based on a series of thermal desorption experiments differing in the original degree of covering of the surface. The original data in this case can be represented in the form of a family of curves (this method is illustrated in Fig.3), each point of which corresponds to a definite rate of the process, temperature, and degree of covering of the surface θ. These data are used to construct desorption isotherms (Fig.3*b*), that is the dependence of W_{des} on θ (or N) for several constant temperatures. These relationships make it possible to determine the order of the process if the data are represented, for example, on coordinates $\ln W - \ln\theta$ (in Fig.3*b* the order of the reaction is 1).

The Arrhenius relationships are then constructed for a series of constant values of the degree of covering (Fig.3c), and finally the dependence of the activation energy on the degree of covering is calculated (Fig.3d). The great advantage of this method is that in the treatment of the data it is not necessary to know beforehand or to assume the kinetic order of the process. Moreover, the form of the $E = f(\theta)$ relationship shows clearly whether the surface is uniform or non-uniform.

Later, it was suggested that the heating rate be varied instead of the initial degree of covering;[14] this makes it possible to cover a wider temperature range for the process, and hence to calculate its kinetic parameters more accurately. It has been pointed out,[15] however, that if both E and k depend on the degree of covering, the dependence of the rate of the process on the concentration of adsorbed substance (Fig.3b) may not reflect the true order of the reaction.

In addition to the above methods for determining the order of the reaction, mention must be made of another method, based on the analysis of the shape of the TD or TPSR peaks. It has been proposed[16] that the order of the desorption be estimated using the so-called "shape index" S, which is the ratio of the slopes of the tangents to the TD peak at the points of inflection on the ascending and descending branches. The values of this parameter were subsequently calculated[8] for four cases: for first- and second-order desorption processes with and without re-adsorption. These calculations[8] were subsequently refined.[17] Here, however, it may be noted that according to the published data,[8] the parameters S for first- and second-order processes in the absence of re-adsorption have different values and are independent of the original degree of covering. At the same time, the values of S are similar for first-order desorption without re-adsorption and for second-order desorption with re-adsorption. This situation makes it difficult to determine the kinetic order of the process; moreover, since graphical differentiation of the TD (or TPSR) peak is necessary, the uncertainty of the determination of the parameter S is high.

The kinetic parameters of the desorption or the surface reaction can be determined using appropriate mathematical programs which make it possible to select these parameters on the basis of a regression analysis to give best agreement with the experimental curve. This method can be used even for overlapping peaks,[18] although it is pointed out[18] that it is difficult to choose between different models. An undoubted advantage of this method is that it is possible to vary the dependence of k and E on the degree of covering; this was clearly demonstrated[19] in an analysis of the experimental TD spectra for but-1-ene from the surface of NaY zeolites.

The principal methods of determining the kinetic parameters of desorption have been examined. The most suitable methods for the treatment of single peaks are apparently the half-width method and the linearisation of the TD curves on Arrhenius coordinates. These methods are simple and sufficiently reliable. If the peaks overlap or if there is extensive non-uniformity of the surface, however, the method of "desorption isotherms" is preferred. Naturally, all the above methods for determining the kinetic parameters of thermal desorption are also applicable when chemical transformations take place on the surface. In this case the kinetic parameters obtained from the curves giving the time (temperature) dependence of the removal of the reaction products reflect both their desorption into the gas phase and the processes taking place on the catalyst surface. Moreover, the TPSR method makes it possible, in particular, to obtain information on the presence of active centres of different types, stepwise mechanisms, the limiting stage of the process, and intermediate compounds.

III. REACTIONS ON CATALYST SURFACES

1. Active Centres of Different Types

In ordinary thermal desorption, when the interaction of the gas with the surface takes place without change in the chemical composition of the particles, the existence of adsorption centres of different types is indicated by the existence of several TD peaks. Similarly, in TPSR, the appearance of several peaks for the same reaction product may indicate non-uniformity of the active surface in the given reaction. In this case, however, there may be several factors responsible for this type of TPSR spectrum, so that additional experiments are required to prove the existence of active centres of different types. This is particularly necessary in the case of deposited catalysts.

Thus if it is assumed that there is only one type of centre on which the reaction takes place, but that the carrier contains pores with different dimensions, then in this case, even if the reaction takes place with the same rate constant on all the active centres, the removal of the products into the reaction space free from catalyst (where the concentration is properly measured) may be determined by the rate of diffusion from different pores and by re-adsorption. Thus the existence of several peaks will indicate not the existence of active centres of different types but a distribution of the pore sizes in the carrier. It is therefore first necessary to estimate the rates of diffusion and adsorption and to be satisfied that these processes do not influence the nature of the TPSR spectrum (the positions and half-widths of the peaks). This can be done experimentally by varying the particle size of the catalyst, the weight of catalyst, and the rate of evacuation (or the velocity of the stream of carrier gas), and hence changing the concentration of the reaction product over the catalyst.

A second and apparently more significant factor responsible for the existence of several peaks for a given product is related to the kinetic characteristics of the reaction. If it is assumed that the reaction on the surface takes place according to the simple scheme A → B → C → D, and if the adsorption of the compound A is carried out at a sufficiently high temperature, then at the start of the actual TPSR experiment the reaction may already have taken place to some extent, and the compounds A, B, and C may be present on the surface in definite concentrations. In this case, when the catalyst is heated, the appearance of the product D in the gas phase will be determined by the rate constants of three corresponding processes, namely A → B → C → D, B → C → D, and C → D, and this may lead to the appearance of several peaks for the product D in the TPSR spectrum. To determine whether this effect is present, it is necessary to carry out the adsorption at different, preferably lower, temperatures. In this case the transformation of the adsorbed substance A into B and C will naturally be hindered, and in the limiting case, only the substance A will be present on the surface at the start of the TPSR experiment. If change in the adsorption temperature does not lead to a decrease in the number of peaks for the product, this indicates that active centres of different types are in fact present on the surface.

Another method for proving the presence of different centres on a catalyst surface is by modifying the centres in some way and then analysing the TPSR spectra. This approach has been used, in particular, in a study[20] of the dehydrocyclisation of n-heptane on deposited platinum specimens with different degrees of dispersion (Fig.4). Fig.4 shows that there is a correlation between the intensity of the high-temperature peak of toluene and the degree of

dispersion of platinum. Thus the TPSR spectrum in this case does in fact characterise the catalyst. This spectrum can be used to determine the kinetic parameters of the process on centres of each type, and their concentration. Thus the TPSR method, in addition to providing a means of investigating the mechanism and kinetics of the reaction being studied, also makes it possible to characterise the catalyst itself.

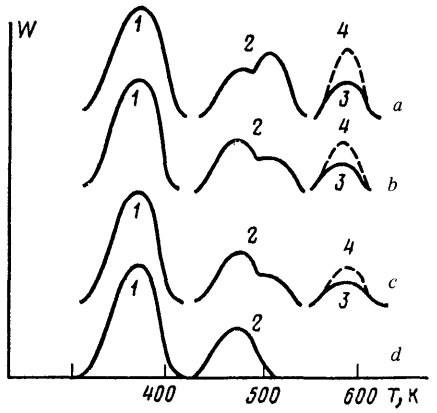


Figure 4. TPSR spectra of n-heptane on Pt/Al_2O_3 specimens with different platinum particle sizes, Å: *a*) 13, *b*) 17, *c*) 38, *d*) 1000; *1*) heptane, *2*) toluene, *3*) benzene, *4*) methane.[20]

2. Stepwise Mechanisms of the Surface Reaction and the Limiting Stage

The advantages of the TPSR method are possibly revealed to the greatest extent in the study of the mechanisms of catalytic reactions. Although such reactions as the recombination-desorption of diatomic molecules naturally are also surface reactions, the application of the TPSR method to more complex processes such as catalytic decomposition, oxidation, dehydrogenation, and dehydrocyclisation will be considered.

A study of the decomposition of hydrazine and ammonia on Ir/Al_2O_3 by the TPSR method and infrared spectroscopy[21] showed that the reaction of hydrazine with the catalyst surface leads to the appearance, in addition to the peaks of the main products, of an additional peak due to nitrogen remaining in the adsorbed state in the atomic form up to high temperatures. The high strength of the bond formed by the nitrogen atoms with the surface was regarded[22] as the factor responsible for the gradual decrease in the activity of the Ir/Al_2O_3 catalyst during the decomposition of N_2H_4 when the process was carried out under stationary conditions. As in the earlier studies,[21] a single nitrogen peak with $T_m \cong 670$ K was observed, whereas the formation of NH_3 takes place chiefly in the temperature range 300–500 K (Fig.5). The appearance of the nitrogen peak with $T_m = 670$ K in the decomposition of both N_2H_4 and NH_3 indicated[22] that the reaction of N_2H_4 with Ir/Al_2O_3 leads to rupture of the N–N bond in the hydrazine molecule.

Even this TPSR study[22] essentially used a procedure involving the preliminary adsorption of possible intermediate compounds (in this case NH_3, which is readily transformed into NH_2). This approach was apparently used in most complete form in studies[23,24] which showed that the principal route in the dehydrocyclisation of C_6–C_7 hydrocarbons on Pt/Al_2O_3 involves the stepwise dehydrogenation of the starting material.

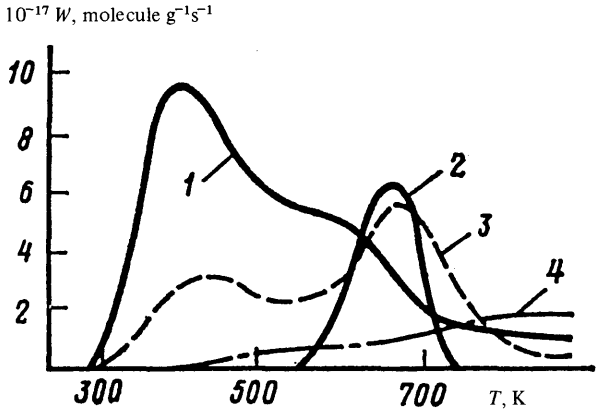


Figure 5. TPSR spectra of N_2H_4 on 0.38% Ir/Al_2O_3 (complete covering by N_2H_4 at 298 K); *1*) NH_3 (rate *W* increased by a factor of 1.3), *2*) N_2 (×2.1), *3*) H_2, *4*) H_2O (×25).[22]

This approach can be examined in slightly more detail. If it is assumed that the reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} C_{gas}$ takes place on the surface and that the limiting stage is the transformation of B into C, then the parameters determined from the peak for the liberation of C into the gas phase should coincide for the adsorption of the substances A or B, but after the adsorption of the substance C the C_{gas} peak should be displaced to lower temperatures. On the other hand, this approach makes it possible to determine the limiting stage of the process. On the other hand, if the rate constants for the formation of C_{gas} from A and from B, determined by the TPSR method, coincide completely, this indicates that B is in fact an intermediate compound in the chain of successive transformations of A into C_{gas}.

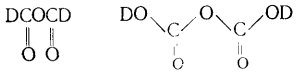
Using this approach, it has been possible to show[23] that the dehydrogenation of cyclohexane on platinum catalysts takes place on centres of two types, corresponding to two benzene peaks (Fig.6). The limiting stage on centres of one type is the transformation of cyclohexane into cyclohexene, and that on the centres of the other type is the desorption of the firmly bound form of benzene.

The question naturally arises of whether the suggested intermediate substances in adsorption give the same surface forms as are produced during the reaction. It is difficult to answer this question unambiguously, and its solution requires the use of other independent methods, for example spectroscopy.

To investigate the reaction mechanism it is important to carry out a complete analysis of the thermal-desorption curves for all the reaction products. A detailed study carried out in this way made it possible[25] not only to determine the mechanism of the decomposition of methanol on pure tungsten but also to follow the change in the mechanism of this reaction as carbon was deposited on the catalyst surface. Other similar examples have been described.[26–29]

In particular, in a study of the decomposition of labelled formic acid DCOOH on a single crystal of nickel,[29] it was

shown (Fig.7) that the decomposition products D_2 and CO_2 are desorbed simultaneously at T_m = 400 K, and that CO is desorbed at higher temperatures (the narrow CO peak in Fig.7 corresponds to a mass-spectrometric fragment of CO_2). The study of the adsorption of carbon monoxide itself showed that CO is desorbed at the same temperatures as the CO obtained by the decomposition of formic acid. The simultaneous removal of CO_2 and D_2 indicates that the desorption of these products is not the limiting stage (otherwise they would have different T_m). Quantitative analysis showed that D_2, CO_2, and CO are liberated in the ratio 1 : 1 : 1. Since H_2O was formed and liberated at much lower temperatures, the following two possible forms were proposed for the adsorbed intermediate, from which the products indicated are obtained:



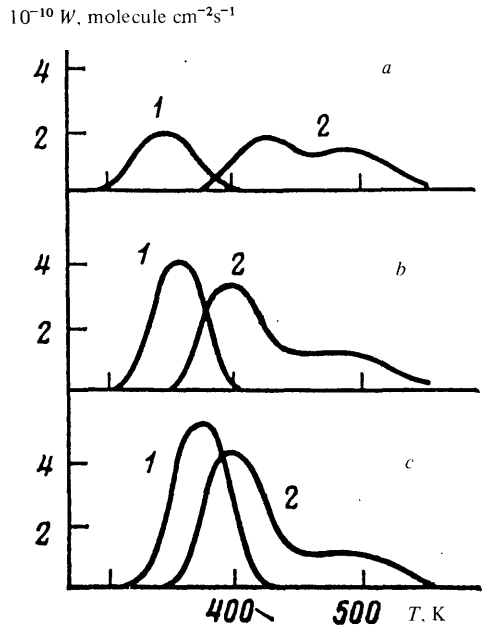


Figure 6. TPSR spectra after the adsorption of cyclohexane (*a*), cyclohexene (*b*), and cyclohexadiene (*c*) on Pt/Al_2O_3: *1*) original hydrocarbon, *2*) benzene.[23]

Labelled molecules were used in this study,[29] although attention was not concentrated on the distribution of isotopes in the reaction products. This approach, however, can give valuable information on the surface process. In a study of the oxidation of ethanol on a single crystal of silver,[29] $^{18}O_2$ and CH_3CH_2OD were used to distinguish the hydrogen joined to hydrogen atoms from the hydrogen in the hydroxyl group. D_2O, H_2, C_2H_4, CH_3CH_2OH, and CH_3CH_2O were detected in the reaction products. The TPSR spectra obtained, and the distribution of the isotopes in the reaction products, led to the following conclusions: 1) on adsorption, the hydroxyl group of the alcohol reacts with the surface ^{18}O atoms to give adsorbed CH_3CH_2O and D_2O; 2) the simultaneous appearance of CH_3CH_2OH, CH_3CHO, and H_2 in the gas phase indicates that all these products are formed from the same intermediate, namely the adsorbed species CH_3CH_2O; and 3) the formation of C_2H_2, $D_2^{16}O$, and H_2 from $CH_3CH_2^{16}OD$ is associated with the decomposition of a surface complex consisting of two alcohol molecules.

An analysis[30] of the liberation of D_2 and deuteriated derivatives of benzene during the dehydrogenation of cyclohexane (C_6D_{12} was used to distinguish the hydrogen liberated from the cyclohexane molecule from the hydrogen adsorbed during the reduction of the catalyst) confirmed the earlier conclusion[23] that this process takes place on centres of two types. On the low-temperature centres the process is limited by the removal of hydrogen, whereas on the high-temperature centres the slowest stage is the addition of surface hydrogen to the dehydrogenated form of benzene.

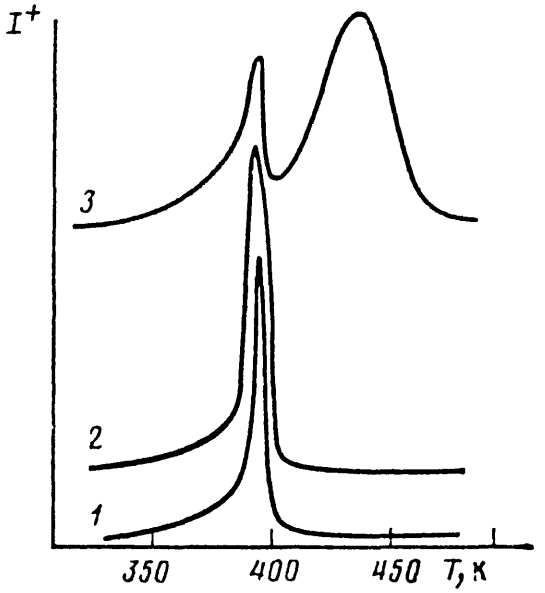
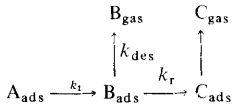


Figure 7. TPSR spectra after the adsorption of DCOOH on Ni(110) at 310 K: *1*) D_2, *2*) CO_2, *3*) CO; I^+ is the mass spectrometer signal.[29]

IV. INTERMEDIATE REACTION PRODUCTS

In the great majority of cases, the intermediate products of the surface reactions are liberated into the gas phase in such small quantities that they cannot be detected by ordinary methods. This is due to the fact that the rate constant of the surface process is generally appreciably greater than the rate constant of the desorption of the intermediate substance. It has been shown,[31-33] however, that if the catalyst surface is heated very rapidly, it becomes possible to observe the intermediate and final reaction products simultaneously. Thus if for example the following transformations take place on the surface



and that the limiting stage is $A_{ads} \rightarrow B_{ads}$, then the liberation of the products B_{gas} and C_{gas} will be determined by the constant k_1. In this case they will appear almost simultaneously, and

the heating rate will have little influence on their relative quantities. If however the surface process is limited by the stage $B_{ads} \rightarrow C_{ads}$, then in this case the relative integral yield of the product B_{gas} will increase sharply with increase in the heating rate. An example is provided in Fig. 8, which gives the dependence of the yield of the intermediate substance on the heating rate for various typical parameters of the separate stages.

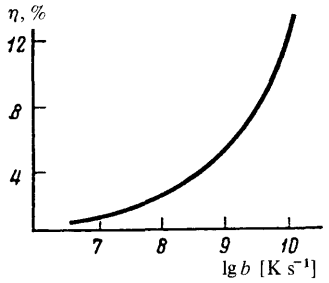


Figure 8. Dependence of the yield of intermediate substance η on the heating rate b at $E_{des} = 63$ kJ mole^{-1}, $E_r = 42$ kJ mole^{-1}, and $k^0_{des}/k^0_r = 10$.[33]

It has been suggested[31,32] that pulse laser sources be used to obtain high heating rates ($b > 10^4$–10^5 K s^{-1}). Because of the finite dimensions of the space of the drift of the desorbed species from the surface being studied to the analyser, the time resolution of the recording systems (mass spectrometers) was worse than 10^{-4}–10^{-5} s, that is the traditional TD or TPSR curves could not be obtained, and the mass-spectrometric analysis made it possible to determine only the integral yield of products. The approach developed in Ref. 33 made it possible to propose a method for determining the kinetic parameters of the desorption of intermediate products, based on the measurement of their integral yields at different heating rates.

Laser-stimulated thermal desorption has been used[34] to detect the intermediate products of the dehydrocyclisation of alkanes. It was shown that in the case of hexane, the reaction involves the intermediate formation of hex-2-ene and hexadiene. The same method has been used[35,36] to study the reaction of acetaldehyde with copper oxide catalysts. The change in the predominant direction of the transformations of the adsorbed species with change in the rate of heating of the catalyst was demonstrated for the decomposition of methanol on a nickel surface.[37] It was shown[37] that during slow TPSR ($b \cong 7$ K s^{-1}), less than 10% of the original methanol is liberated into the gas phase (in this case it must be regarded as an intermediate product), and the rest is in the form of H_2 and CO. In the case of laser TPSR, however, the opposite picture is observed, that is the chief product after the adsorption of methanol at low temperatures is CH_3OH.

The use of pulse lasers with a high quantum flux density per unit surface area can in principle lead to effective decomposition of the species on the surface. To verify this it is necessary to carry out additional experiments, as for example in a comparison[34] of the effect of laser radiation on hexane adsorbed on a Pt/Al_2O_3 catalyst and on the Al_2O_3 carrier. The decomposition of hexane was slight in both cases, but the liberation of reaction products, namely benzene, hexene, and hexadiene, was observed only in the experiments with Pt/Al_2O_3. These data indicate that a catalytic process is taking place, and that there are no chemical transformations of the molecules in the gas phase directly under the influence of the laser radiation.

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The material reviewed showed that the TPSR method can be used to determine the kinetic parameters of a surface process and its limiting stage, to reveal non-uniformity of catalyst surfaces, and in a whole series of cases to establish the reaction mechanisms. Additional information can be obtained by combining the TPSR method with, for example, infrared spectroscopy or other methods for studying surfaces.† It is always necessary, however, to take account of a characteristic feature of TPSR, namely the absence of the original compounds from the gas phase. Thus when transferring data obtained by the TPSR method to ordinary catalysis, care is required, and it is necessary in every case to be satisfied that the introduction of the original substances into the gas phase does not change the reaction mechanism.

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† See also the review by O.V.Krylov and A.D.Berman in this issue of the journal.

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