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PULSE CHROMATOGRAPHIC METHOD FOR THE INVESTIGATION OF CATALYTIC REACTIONS

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SUMMARY

A short survey is given of the application of the pulse chromatographic method in the study of the kinetics of catalytic reactions. A new method for studying the kinetics of adsorption during catalytic processes is described, based on the analysis of the shapes and retention times of peaks of reactants and products at the reactor outlet. This method was tested for the model reaction of cumene cracking over a silica–alumina catalyst.

A theory was derived for pulse poisoning of the catalyst surface with a reversible poison. The proposed theory was verified experimentally for the model reaction of cumene cracking over a silica–alumina catalyst by poisoning it with pyridine.

INTRODUCTION

A reactor and a chromatographic column connected in series are commonly used for chromatographic studies of catalytic reactions. The size and shape of the reactant and product peaks in the chromatograms show the kinetics of the processes that take place in a catalytic reactor. Essentially the same experimental technique is used in analytical reaction chromatography. In both instances, two processes are responsible for the final results obtained, *viz.* the chemical reactions and chromatographic separation. It can therefore be suggested that the theories for both processes must be similar and that the conclusions are of interest not only for specialists in catalysis but also for those engaged in analysis and chromatography. However, catalysis studies require information on the reaction kinetics and mechanism, whereas conditions that ensure that the kinetics have only a small effect on chromatographic separation are needed for reaction chromatography.

The present paper consists of two parts. The first is a short review of catalytic processes in pulse micro-reactors, and the second contains some examples of the application of pulse micro-reactors to the calculation of the rate constants of some catalytic reactions. A pulse method for the study of poisoning of the catalyst surface is described at the end of the paper.

THEORETICAL

As in chromatography, all research on the theory of chemical processes in micro-reactors can be classified into two large groups. The first involves the rapid attainment of adsorption equilibrium, and the second takes into consideration the rate of attaining equilibrium between gases and solids. However, classification based on the shape of the adsorption isotherm is more expedient for representing the kinetics of catalytic processes. Most experiments are concerned with linear isotherms but certain research on processes showing curved isotherms has been reported within the last few years[1].

The nature of adsorption equilibria and the kinetics of adsorption have a different effect on the degree of conversion, depending on the reaction order and its specific mechanism.

The brief summary of the theory of processes in micro-catalytic reactors can first be illustrated with a simple case, in which adsorption of the reactant A on the catalyst surface is very fast and obeys Henry's law. The effect of diffusion on broadening of the band can be neglected. Such a case for a first-order reaction was considered in the well-known paper by BASSETT AND HABGOOD[2], who derived the following equation:

$$k\Gamma = \frac{1}{\tau} \ln \left(\frac{1}{1-\alpha}\right) \tag{1}$$

where k is the rate constant of the reaction, Γ is Henry's coefficient, τ is the contact time and α is the degree of conversion.

Eqn. 1 permits the apparent rate constant of the reaction to be calculated. It is important for such a model that the reactant peak width does not change during the course of the reaction and that the peak height decreases exponentially with time. The degree of conversion does not depend on the shape of the pulse entering the reactor. A different situation is observed for the product peak[3] (Fig. 1). The band on the right in Fig. 1 refers to reactant A.

The right-hand boundary of the band of product B joins the band of reactant A and moves at the same velocity as that of A; the left-hand boundary of the band of product B moves at a velocity determined by the magnitude of the factor Γ_B. Thus the width of the band of product B can be calculated from the difference $\Gamma_A - \Gamma_B$, and its shape from the rate constant of the catalytic reaction.

Some expressions were obtained for the calculation of the rate constant of the

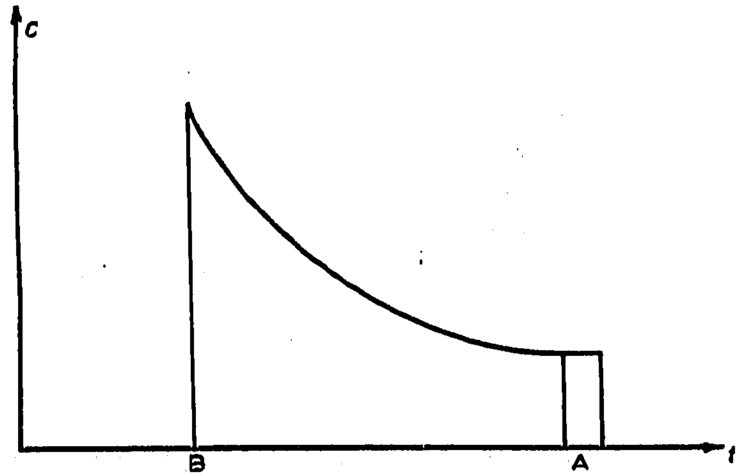


Fig. 1. Theoretical chromatogram, obtained directly at the reactor outlet, for the reaction A → B.

catalytic reaction by using the peak shape and the retention time[4]. The equations obtained were verified experimentally for the dehydrogenation of cyclohexane on a Pt/Al_2O_3 catalyst. All the calculations were carried out by making use of the hydrogen peak.

The irreversible reaction of the nth order with a linear adsorption isotherm of reactant A and rapid attainment of adsorption equilibrium have been examined earlier[5]. The following equation for the product A elution curve was derived:

$$c_A(l,t) = \frac{\psi(t - t_A^{\text{ret}})}{\sqrt[n-1]{1 + (n-1)kt_A^{\text{ret}}\Gamma_A^{n-1}[\psi(t - t_A^{\text{ret}})]}} \tag{2}$$

where $\psi(t - t_A{}^{\text{ret}})$ is the pulse shape, l is the reactor length and $t_A{}^{\text{ret}}$ is the retention time of reactant A.

The degree of conversion for any reaction order can be calculated by making use of eqn. 2. If the reaction order is known, it is possible to calculate the rate constant for any pulse shape.

The order of reaction, n, is seldom known, but it can be determined from experiments with low degrees of conversion. This was proposed by the authors of the differential chromatographic method[6]. The reaction rate, w, can be related to average pulse concentration, c_{av}, which can be determined from the pulse shape. Then w can be calculated from the equation:

$$w = \frac{\Delta m}{\Delta t V_{\text{cat}}} = k_{\text{eff}}\Gamma^n\, c_{\text{av}}^n \tag{3}$$

where Δm is the amount of converted reactant A, Δt is the time of contact and V_{cat} is the catalyst volume.

It can be seen from eqn. 3 that n can be calculated from the slope of the straight line of log w against log c_{av}, and k_{eff} from the intercept on the ordinate. In order to calculate the true rate constant, k_{tr}, it is necessary to introduce a correction that takes into account the pulse shape, $\psi(t)$, at the reactor inlet:

$$k_{\text{tr}} = k_{\text{eff}} \frac{\left[\frac{1}{T}\int_0^T \psi(t)\mathrm{d}t\right]^n}{\frac{1}{T}\left[\int_0^T \psi^n(t)\mathrm{d}t\right]} \tag{4}$$

It follows from eqn. 4 that when $n = 1$ and $n = 0$ the correction is unity. It can be shown that when the reactant pulse is rectangular, the correction is also unity. The effect of diffusion on the reaction of the type $n\text{A} \rightarrow \text{B}$ has been studied earlier[7]. It was found that broadening of the A band corresponds to slowing down of the reaction. This effect is stronger for larger values of n.

It was reported in the literature that the rate of attainment of adsorption equilibrium was commensurable to the rate of the catalytic reaction. The possibility of calculating rate constants for adsorption and desorption is discussed below. The effects of longitudinal and internal diffusion on an irreversible first-order reaction have been analysed elsewhere[8,9].

The simultaneous treatment of adsorption kinetics and the longitudinal and internal diffusion involves considerable mathematical difficulties. Therefore, attempts were made[10,11] to solve this problem by means of the plate theory, which is well known in chromatography. This theory does not elucidate in detail the mechanism of complex processes in a reactor, but allows the effect of some experimental parameters on retention time and on the shape of bands of reactants and products to be determined. Although such an approach is less rigorous, the results that can be obtained give all the qualitative relationships, taking into account the kinetics and diffusion. The use of equations from the plate theory by NAKAGAKI AND NISINO[11] made it possible to calculate from a catalytic chromatogram the rate constant for the catalytic isomerization of cyclopropane to propylene on molecular sieve 13 X with some cations replaced by Ni^{2+}.

Some specific features responsible for the rate of a heterogeneous reaction must be taken into account when investigating reversible reactions in a micro-catalytical reactor. The most important factor seems to be the possibility of separating reactants and products on the catalyst layer during the course of a catalytic process. Obviously, for reversible reactions of the type $A \rightleftarrows B + C$, spatial separation of B and C will induce a change in the degree of conversion of A as a result of partial or full inhibition of the reverse reaction[12].

In the case of consecutive reactions[13,14], for example those of the type $A + B \rightarrow R$ and $R + B \rightarrow S$, the separation of B and R will result in a decrease in the yield of S and in an accumulation of the intermediate product R.

This effect depends on the pulse width at the inlet, as its decrease intensifies separation. In the case of a reaction of the type $A \rightarrow R$ and $2R \rightarrow S$ such an effect can arise from the difference in the adsorption coefficients of reactant A and the intermediate product R.

The product band broadens and hence the rate of the second reaction decreases with increasing difference in the adsorption coefficients.

The reaction of the type $A \rightleftarrows B$ can be treated in a similar manner. Owing to the difference in the adsorption coefficients of A and B, the rate of the reverse reaction will decrease. It was found[7] that the same effect is possible as a result of diffusion when the adsorption coefficients of A and B are equal. The Langmuir isotherm of adsorption has been analysed[1], and it was found that with the rapid attainment of adsorption equilibrium the degree of conversion for the reaction $A \rightarrow B$ increased compared with that in a flow reactor, as the reactant band becomes diffuse owing to the non-linear adsorption isotherm, and inhibition decreases and the true retention time of molecular residence in the reactor increases.

The situation will be more complicated for a reversible reaction, for example of the type $A \rightleftarrows R + S$, in which the degree of conversion will increase as a result of the difference $\Gamma_R - \Gamma_S$ and of the reactant band broadening due to the non-linearity of the isotherm. The broadening of peaks R and S must hinder the separation and increase the rate of the reverse reaction. The quantitative results will depend on the actual value of the adsorption coefficient.

The case when the attainment of equilibrium is slow is very interesting. In this case, the difference between the results obtained by pulse and flow methods will be even greater because of the different degrees of coverage of the catalyst surface. As the front part of the pulse is moving over a clean surface, with a narrow pulse the coverage can be less than in the case of a flow reactor. BETT AND HALL[15] have shown that in some cases, when equilibrium is not attained, certain reaction steps can occur in time intervals between the pulses, which complicates the interpretation of the results. It is evident that the differences in surface coverages must change the kinetic regularities, reaction orders, etc.

Several examples of catalytic reactions studied by the chromatographic method are given below.

When the rate of attainment of adsorption equilibrium is commensurable to the rate of a catalytic reaction, the pulse chromatographic method gives information about the kinetics of adsorption of the reactants and products[16]. Valid solutions can be obtained here only with linear isotherms. Equations were derived relating the degree of conversion, α, the retention time, t_{ret}, and the broadening of the peaks, σ^2, of reactants and products with constants of adsorption, k^a, of desorption, k^d, and the reaction rate constant, k. For an initial reactant these equations will be:

$$\ln\left(\frac{1}{1-\alpha}\right) = \frac{l}{u}\cdot\frac{(1-\varkappa)k^a k}{k+k^d} \tag{5}$$

$$t^{\mathrm{ret}} = \frac{l}{u}\left[\varkappa + \frac{(1-\varkappa)k^a k^d}{(k+k^d)^2}\right] \tag{6}$$

$$\sigma^2 = \frac{2l}{u}(1-\varkappa)\cdot\frac{k^d k^a}{(k+k^d)^3} \tag{7}$$

where $\varkappa$ is the catalyst porosity and u is the linear velocity of the flow. In all three equations, the values α, t_{ret} and σ^2 are linearly dependent on $1/u$. The k^a, k^d and k values can be calculated from experimental α, t_{ret} and σ^2 values, making use of eqns. 5 and 7.

The principal difficulty consists in the determination of t_{ret} and σ^2 directly at the reactor outlet. Separation of the components to a sufficient degree for measurement of t_{ret} and σ^2 seldom occurs on the catalyst layer. A simple method for the determination of these values has been proposed by us, involving the measurement of $t^{\mathrm{ret}}_{\mathrm{sum}}$ and σ^2_{sum} of the peak of the reactant which has passed through the system consisting of the reactor and the chromatographic column.

Furthermore, it is necessary to determine σ^2_{col} and $t^{\mathrm{ret}}_{\mathrm{col}}$ when the reactant or product is admitted directly into the chromatographic column. Then the values of $\sigma^2_{\mathrm{react}}$ and $t^{\mathrm{ret}}_{\mathrm{react}}$ can be calculated using the following simple equations:

$$\sigma^2_{\mathrm{react}} = \sigma^2_{\mathrm{sum}} - \sigma^2_{\mathrm{col}} \tag{8}$$

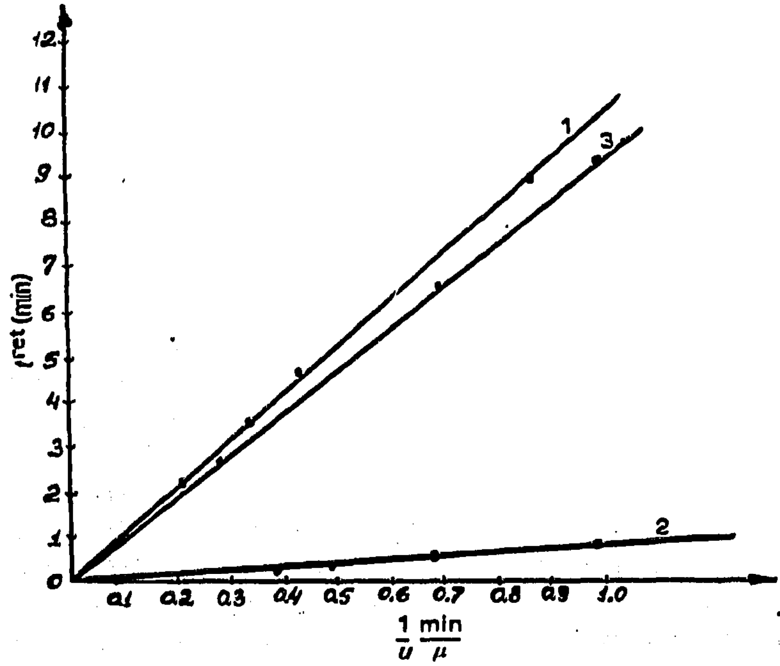
$$t^{\mathrm{ret}}_{\mathrm{react}} = t^{\mathrm{ret}}_{\mathrm{sum}} - t^{\mathrm{ret}}_{\mathrm{col}} \tag{9}$$

EXPERIMENTAL INVESTIGATION OF THE ADSORPTION KINETICS OF CATALYTIC PROCESSES

The above method was tested for a model reaction involving the cracking of cumene over a silica–alumina catalyst. Fig. 2 is a typical graph of the retention time of cumene in the reactor as a function of $1/u$. The assumption that the adsorption isotherm is linear is seen to be confirmed by experiment. Similar dependences were obtained for α and σ^2.

Table I lists calculated k^a, k^d and k values for different temperatures. Here $\mathrm{tg}\varphi_1$, $\mathrm{tg}\varphi_2$ and $\mathrm{tg}\varphi_3$ are tangents of the slopes of dependences t^{ret}, $\log\,(1/(1-\alpha))$ and σ^2 from $1/u$. The activation energies for reaction, adsorption and desorption were calculated from the temperature dependences of k^a, k^d and k. The activation energy of the reaction was found to be 23 kcal/mole, and adsorption proceeded with almost zero activation energy. This is in good agreement with the available data[17].

Fig. 3 shows a chromatogram measured directly at the reactor outlet after admission of a cumene pulse. Two peaks can be seen. Peak 1 refers to unconverted cumene and peak 2 to the products, benzene and propylene. The separation of reactants and products is seen to occur actually on the catalyst layer. Fig. 4 shows a chromatogram obtained for a mixture of cumene with benzene. It can be seen that along with the cumene and product peaks (peaks 1 and 2), an additional peak, identified as that of benzene, occurs. The movement of the peak of benzene as a



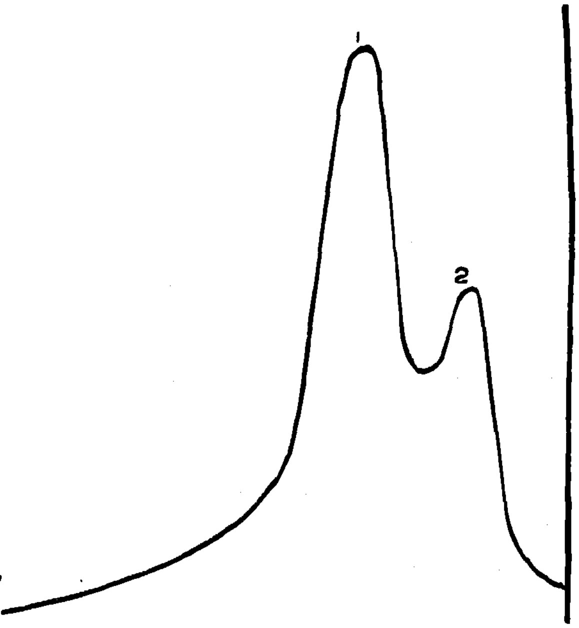


Fig. 2. Retention time of cumene on a silica–alumina catalyst as a function of $1/u$. 1 = Measured retention time; 2 = retention time of air; 3 = corrected retention time.

Fig. 3. Catalytic chromatogram obtained by introducing cumene into the reactor.

TABLE I

CALCULATION OF RATE CONSTANTS USING THE PEAK OF CUMENE

Temperature (°C)	$\mathrm{tg}\varphi_1$	$2.3\cdot\mathrm{tg}\varphi_2$	$\mathrm{tg}\varphi_3$	$k + k^d$ (*min*$^{-1}$)	k/k^d	k (*min*$^{-1}$)	k^d (*min*$^{-1}$)	k^a (*min*$^{-1}$)	Γ (*ml/ml catalyst*)
270	8.8	0.69	0.97	18.2	0.0044	0.08	18.12	600	33
280	7.5	0.83	0.70	21.4	0.0052	0.12	21.28	570	26.8
290	7.0	1.09	0.63	22.2	0.0070	0.15	22.05	560	25.5
300	6.5	1.32	0.53	24.5	0.0084	0.21	24.29	590	24
340	3.1	2.8	0.13	47.5	0.018	0.85	44.65	600	13.5

product along the catalyst layer is therefore slower than that of benzene admitted directly into the reactor. This displacement is presumably connected with the course of the catalytic reaction.

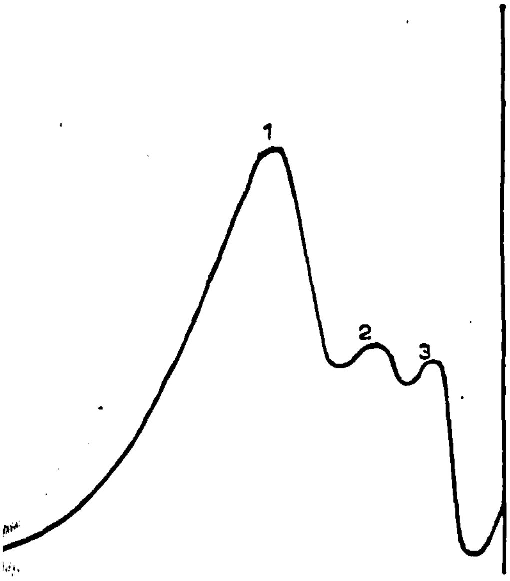
These experiments have therefore proved in principle the possibility of obtaining very important information about the rate constants of adsorption and desorption of reactants and products from the shapes and retention times measured directly at the reactor outlet.

Determination of basic paths of complicated catalytic conversions

Another application of pulse chromatography involves the determination of the basic paths of complicated catalytic conversions. In such cases, it is difficult to obtain detailed information about individual steps of the reaction. However, the chromatographic method allows the rates of many single reactions involved in the over-all process to be calculated.

It was shown in studying the oxidative dehydrogenation of butenes[18] that the over-all processes can be represented by the scheme shown in Fig. 5. The oxidative dehydrogenation of the individual isomers of butene is seen to be accompanied by their isomerization. It can be suggested from preliminary experiments[18] and available data[19,20] that all these reactions are first order for butene and zero order for oxygen. The experiments consisted in measuring kinetic curves for pure isomers. A system of differential equations has been derived and solved by us with the aid of a computer. Eight constants of mutual conversion were calculated from the condition of proximity of experimental and calculated curves.

It should be mentioned that a mathematical model is not always adequate for obtaining a clear and reliable basis for discriminating between different schemes for complex processes. Additional information that is used for the rejection of certain hypothetical schemes can be very useful. In order to choose the most probable scheme



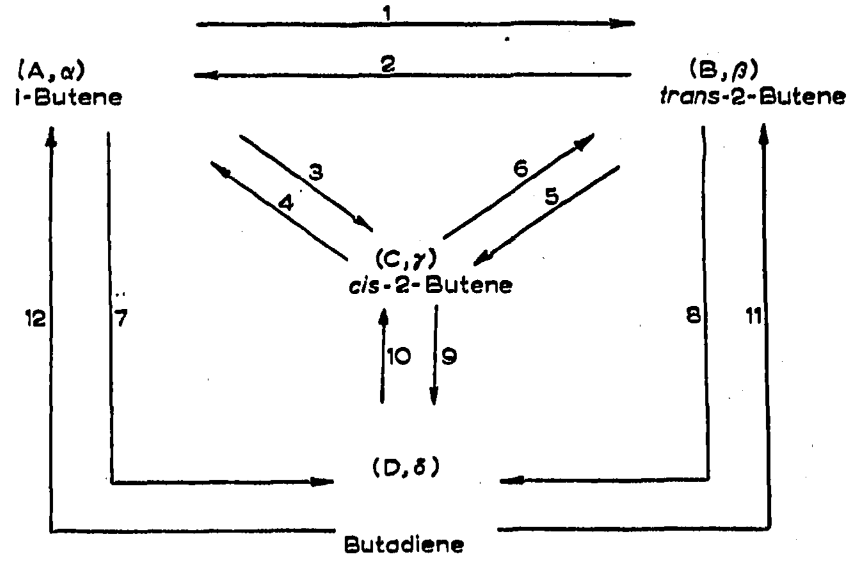


Fig. 4. Catalytic chromatogram obtained by introducing a mixture of cumene and benzene into the reactor.

Fig. 5. Scheme for conversions of 1-butene by oxidative dehydrogenation on Bi–Mo oxides.

of reaction, it is necessary to investigate the agreement between the chosen model and the experimental results over a wide range of experimental conditions. In this sense, great opportunities are provided by a combination of a pulse chromatographic reactor with the radiochromatographic method. Radiochromatography has been used for defining more precisely the above scheme (Fig. 5) of oxidative dehydrogenation of butenes to butadiene over a Bi–Mo catalyst[18].

If α, β, γ and δ are designated as the specific radioactivities of 1-butene, *trans*-2-butene, *cis*-2-butene and butadiene, then, according to the NEUMAN kinetic isotopic method[21], the variations of α, β, γ and δ with time will be expressed by four equations:

$$\frac{d\alpha}{dt} = \frac{1}{[A]} \{k_4[C](\gamma - \alpha) + k_2[B](\beta - \alpha)\} \tag{10}$$

$$\frac{d\beta}{dt} = \frac{1}{[B]} \{k_1[A](\alpha - \beta) - k_6[B](\beta - \gamma)\} \tag{11}$$

$$\frac{d\gamma}{dt} = \frac{1}{[C]} \{k_3[A](\alpha - \gamma) + k_5[B](\beta - \gamma)\} \tag{12}$$

$$\frac{d\delta}{dt} = \frac{1}{[D]} \{k_7[A](\alpha - \delta) + k_8(\beta - \delta)[B] + k_9[C](\gamma - \delta)\} \tag{13}$$

The system of eqns. 10–13 was solved together with that of equations for the material balance, and the rate constants of the elementary reactions were computed, taking into account the resemblance between the experimental curves and those calculated for variations in concentrations and specific radioactivities.

Comparison of experimental and calculated specific radioactivities of components for different times of contact showed fair agreement. Table II lists the values of nine rate constants of single reactions in the oxidative dehydrogenation of butenes to butadiene at temperatures of 310, 396, 436 and 496°.

The oxidative dehydrogenation of 1-butene is seen to proceed faster than that of the other isomers.

The above results seem to show great possibilities, obtained by combining the computerized calculation of kinetic data obtained by a micro-catalytic method with a continuous correlation of the values obtained by radiochromatography. The micro-

TABLE II

CALCULATED RATE CONSTANTS OF SINGLE REACTIONS IN THE OXIDATIVE DEHYDROGENATION OF BUTENES ON Bi AND Mo OXIDES AT DIFFERENT TEMPERATURES

Constants (sec^{-1})	*Temperature (°C)*			
	310	*396*	*436*	*496*
k_1	4	9	15	18
k_2	3	6	7	10
k_3	6	11	11	17
k_4	6	7	8	9
k_6	10	13	14	16
k_7	4	19	33	69
k_8	1	1	3	17
k_9	1	3	7	23

catalytic method provides the possibility both of studying the kinetics of chemical reactions and of investigating the active surface properties. A further example given below shows some recent results obtained in our laboratory by the pulse method on the reversible poisoning of catalytic surfaces.

Reversible poisoning of catalytic surfaces

The usual technique involves the pulsed admission of a certain dose of poison into the flow of the carrier gas. The reactant is also periodically injected into the reactor and variations in the catalyst activity with time under constant experimental conditions are studied. It is natural to suppose that the poison band will migrate along the catalyst layer according to the law of non-linear chromatography[22,23]. The poison will gradually disappear when the poison band reaches the end of the catalyst layer.

The following model was used to describe this process. The catalyst surface was assumed to be homogeneous and to contain adsorption sites both catalyzing the reaction and being inert to it. It was also suggested that adsorption of poison molecules was stronger than that of the reactant molecules and therefore the distribution of poison in the catalyst layer had no time to change within the short period when the reactant band passed through the reactor.

With the above assumptions, the following set of equations can be written:

$$\frac{\partial \theta_c}{\partial t} + \frac{\partial c}{\partial t} - \frac{\partial \theta_a}{\partial t} + u\,\frac{\partial c}{\partial x} + k\theta_c = 0 \tag{14}$$

$$\frac{\partial \theta_c}{\partial t} = k^a[1 - \theta_{c,p}(x)]c - [k^d\theta_c + k] \tag{15}$$

$$\frac{\partial \theta_a}{\partial t} = k_0{}^a c[1 - \theta_{a,p}(x)] - k_0{}^d\theta_a \tag{16}$$

where θ_a and $\theta_{a,p}$ are the areas of adsorption sites covered with molecules of the reactant and of the poison; c is the concentration of the reactant in the gas phase; θ_c and $\theta_{c,p}$ are the areas of active sites covered with molecules of the reactant and of the poison, respectively; k, k^a and k^d are the rate constants of the heterogenous reaction, adsorption and desorption on active sites, and $k^a{}_0$ and $k^d{}_0$ are the rate constants of adsorption and desorption on sites that do not catalyse the reaction. The degree of conversion, α, can be written as:

$$\alpha = 1 - \exp - \left\{\frac{l}{u}\cdot\frac{kk^a}{k + k^d}\cdot\frac{1}{l}\int_0^l [1 - \theta_{c,p}]\mathrm{d}x\right\} \tag{17}$$

where l is the reactor length. Taking log $(1/(1 - \alpha))$ as a measure of the activity, A_g, for poisoning, the relative activity, A_g/A_0, of the catalyst will be determined by the mean value of the coverage of the active sites with poison molecules:

$$\frac{A_g}{A_0} = \frac{1}{l}\int_0^l [1 - \theta_{c,p}(x,t)]\mathrm{d}x \tag{18}$$

As $\theta_{c,p}$ depends on time t elapsed after admission of the poison into the reactor, the relative activity will also be time-dependent. In order to calculate the curves for variations in relative activity with time, it was necessary to suggest a mechanism for the movement of the poison band over the catalyst layer and the law of poisoning.

It was assumed that the adsorption equilibrium for the poison was attained rapidly and that the shape of the band and hence the term $\theta_{c,p}(x,t)$ in eqn. 18 could be calculated making use of equations derived by VAULT[22] and WEISS[23]. Two possible cases were analysed[24]:

(1) The linear law of poisoning, in which one molecule of poison is assumed to remove one catalytic site.

(2) The exponential law of poisoning, in which one catalytic centre can adsorb several molecules of poison.

The second case will be considered in detail.

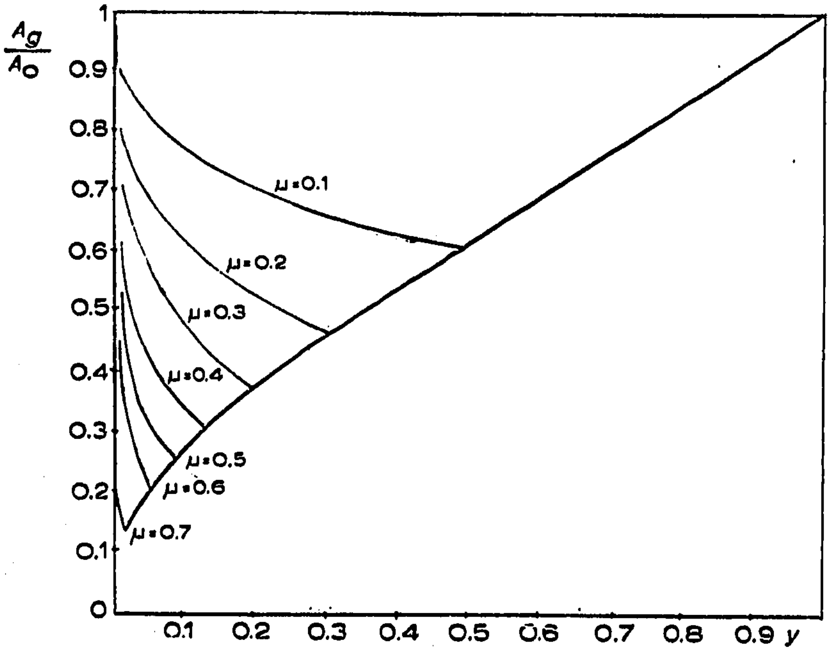


Fig. 6. Calculated curves of poisoning for $\nu = 2$ and $\beta = 10$. Values of μ are shown on the curves.

Fig. 6 shows a set of calculated curves for variations in the relative activity, A_g/A_0, with time for different doses of poison. The $y = t/t_{\text{max.}}$ value was plotted on the abscissa, where $t_{\text{max.}}$ is the time for complete catalyst regeneration. The parameter $\mu = m/q_{\text{max.}}$ represents the dose of poison in milligrams introduced into the reactor, where $q_{\text{max.}}$ is the amount of poison necessary for monolayer surface coverage. It can be seen that the relative activity at first sharply decreases, then passes through a minimum, and finally slowly increases. The greater the dose of poison, the lower is the minimum and the faster it is reached. It will be noted that at a certain time the ascending branches for different doses of poison coincide. The decreasing branch of the curve in Fig. 6 can be described by the equation:

$$\frac{A_g}{A_0} = y + (\sqrt{\mu} + \sqrt{y})^2 + \int_{y}^{\sqrt{y}+\sqrt{\mu}} \exp - \left[\nu_c \frac{\beta\left(\sqrt{\frac{z}{y}} - 1\right)}{1 + \beta\left(\sqrt{\frac{z}{y}} - 1\right)} \right] \mathrm{d}z \qquad (19)$$

$z = x/l$, where l is the length of the column.

The following correlation is valid for the ascending branch:

$$\frac{A_g}{A_0} = y_0 + \int_y^1 \exp - \left[\nu_c \frac{\beta\left(\sqrt{\frac{z}{y}} - 1\right)}{1 + \beta\left(\sqrt{\frac{z}{y}} - 1\right)} \right] \mathrm{d}z \tag{20}$$

ν_c is the number of poison molecules adsorbed by one of the catalytic sites and $\beta = b_k/b_{\mathrm{av}}$, where b_k is the adsorption coefficient of the poison on the catalytic site and b_{av} is the average adsorption coefficient, taking into account the catalytic and adsorption sites.

Calculation gives a simple possibility of determining the number of active sites from the position of minimum $y_{\mathrm{min.}}$ on the curve of relative activity as a function of time, using the expression:

$$q_{\mathrm{max.}} = \frac{m}{(1 - \sqrt{y_{\mathrm{min.}}})^2} \tag{21}$$

The average adsorption coefficient, b_{av}, can be determined from $t_{\mathrm{max.}}$, the time necessary for complete regeneration of the catalyst layer, by making use of the expression:

$$b_{\mathrm{av}} = \frac{vt_{\mathrm{max.}}}{q_{\mathrm{max.}}} \tag{22}$$

where v is the flow-rate of the carrier gas. The curves with different parameters β and b_{av} have been calculated, and comparison of these curves with the experimental ones enable the values of these parameters to be obtained. Knowing β and b_{av}, it is possible to calculate the adsorption coefficients of poisons on the catalytic active sites.

The proposed theory was verified for the model reaction of cumene cracking over a silica–alumina catalyst by poisoning it with pyridine. Fig. 7 shows a comparison of the calculated and experimental curves. The calculated curves are represented by solid lines and fit the experimental results fairly well. As stated above, $q_{\mathrm{max.}}$, the amount of poison needed for complete coverage of the catalyst surface with a mono-

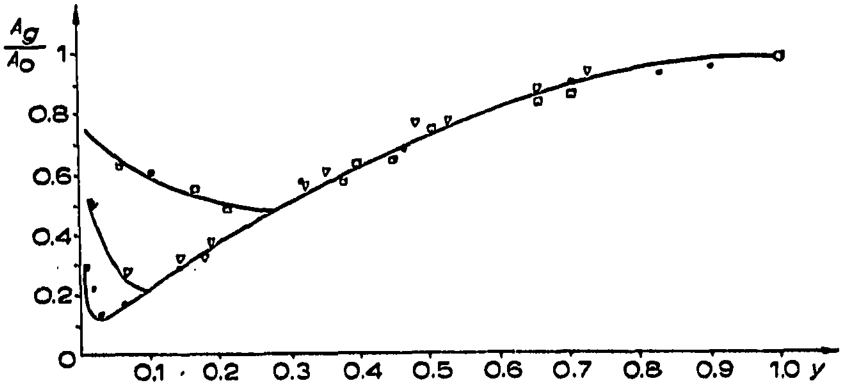


Fig. 7. Comparison of calculated and experimental curves for a temperature of 400°. The solid curves were obtained by calculation with an electronic computer. The points refer to experiments with different doses of poison: □, 0.83 mg; ▽, 1.38 mg; ●, 2.06 mg.

layer, can be determined by using eqn. 21 from the position of $y_{\text{min.}}$ on the curves of relative activities as a function of time for different doses. The value of $q_{\text{max.}}$ appeared to be 2.75 mg/g.

After the experimental determination of $t_{\text{max.}}$, the time necessary for full regeneration, the average adsorption coefficient, b_{av}, was calculated by using eqn. 22. At 400°, b_{av} was 4.8×10^3 ml/mg.

It appeared from a comparison of theoretical and experimentals reults that the most probable value of $\beta = b_c/b_{\text{av}}$ is 2, where b_c, as mentioned above, is the coefficient of adsorption of pyridine on the active sites of the catalyst surface. Poison is therefore adsorbed more readily on active site centres. By making such calculations for different temperatures, it was determined that the heat of adsorption of poison on active sites is $Q_{\text{pois}}^{\text{ads}} = 50$ kcal/mole. This value is a fair agreement with values reported in the literature[25]. We have assumed, on the basis of the described model, that the poison band moving along the catalyst layer obeys the law of ideal chromatography and the Langmuir adsorption isotherm.

Direct proof of these assumptions was of interest. Therefore, the parameters of the Langmuir equation for the poison, derived from the variation of relative activity with time, were compared with those of the isotherm obtained by direct adsorption measurements.

The isotherms of adsorption were calculated from elution curves that were measured by means of a flame-ionization detector.

After integrating the elution curves[26], we calculated the isotherm for pyridine adsorption (points in Fig. 8); from catalytic experiments we found that $q_{\text{max.}}$ corresponds to monomolecular coverage of the catalyst surface ($q_{\text{max.}} = 2.75$ mg/g) and the average adsorption coefficient, b_{av}, of the poison ($b_{\text{av}} = 4.8 \times 10^3$ ml/mg).

Knowing these values, the equation for the adsorption isotherm can be written as:

$$f(c) = \frac{4.8 \cdot 10^3 \cdot 2.75 \cdot C}{1 + 4.8 \cdot 10^3 C} \tag{23}$$

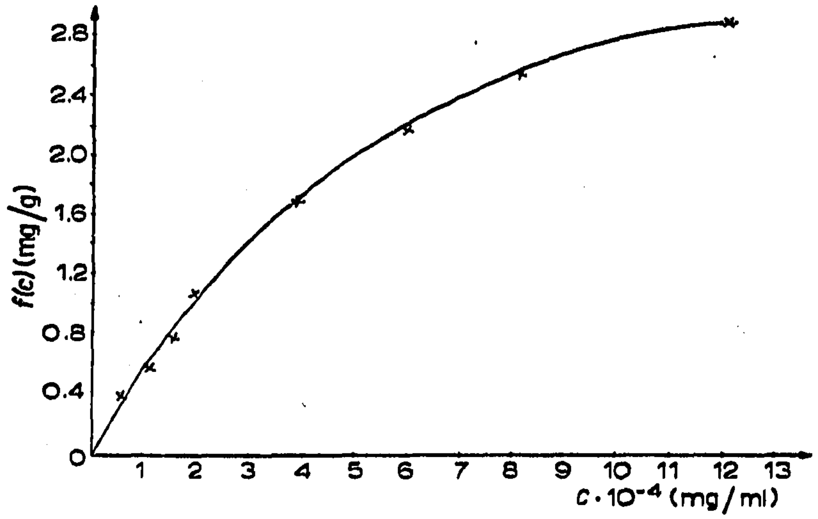


Fig. 8. Comparison of the pyridine adsorption isotherm obtained by measuring the time-dependence of catalytic activity (solid curve) with adsorption measurements (points).

where c mg/ml is the concentration of poison and $f(c)$ mg/g is the amount of pyridine adsorbed.

The isotherms are seen to coincide quite well. Some deviations are noticeable within the range of rather high surface coverage, possibly because the assumptions made in the calculation are not fulfilled for high coverages. But, in general, it can be considered that the coincidence of the isotherms obtained by the two methods proves the validity of the model chosen.

CONCLUSIONS

The above results illustrate the great possibilities opened up by chromatographic methods for the investigation of catalysts and catalytic processes. It has shown, for example, that rather simple measurements of variations in relative activity with time give the possibility of obtaining important information about the number of adsorption sites, the relative strength of adsorption on different sites of the catalyst, etc., that cannot be obtained by the usual methods.

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