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Comparison of the Activities of Catalysts for Heterogeneous Catalytic Reactions

A.V.Sagalovich and A.L.Klyachko-Gurvich

The existing methods for comparing catalytic activities in terms of various parameters of the kinetic equation and the Arrhenius equation are discussed. A criterion is proposed for estimating the reliability of the results obtained by these methods. The conditions for and limits of their applicability have been defined.
The bibliography includes 157 references.

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1. REACTION RATE AS A MEASURE OF CATALYTIC ACTIVITY

Despite its wide employment in studies on catalysis, the term "catalytic activity" is exceptionally indeterminate, since various kinetic parameters are used, and not always justifiably, as a measure of activity. In some reports it is actually not stated at all what is meant by this term. To accord with the significance of the phenomenon of catalysis, the change in the rate of chemical reaction as the result of the introduction of the catalyst into the system should be adopted as a measure of catalytic activity[1]. Since the rate of the non-catalysed process is usually negligibly small compared with the catalysed rate, the rate of reaction in the presence of the catalyst may be regarded as an accurate measure of activity[1-4].

We shall define the rate of a heterogeneous catalytic reaction as a change in the number of reactant or product molecules per unit time per unit catalyst surface. On the basis of this definition, we shall examine the expressions for the rate of reaction in reactors with stationary catalyst beds. Under steady-state conditions in an ideal-mixing flow reactor (a gradient-free reactor, in particular a stirred flow reactor), the rate of reaction is constant both with respect to time and over the entire catalyst surface. If the amount of substance i changes by ΔN_i moles in a stream of reaction mixture passing through a catalyst bed with a surface area S during a time t, the rate of reaction is

$$v = \pm \frac{\Delta N_i}{St}, \qquad (1)$$

where the sign depends on whether the substance i is formed or consumed. When the rate of reaction is expressed in terms of various components of the reaction mixture, account must be taken of the stoichiometric coefficients. In a static ideal-mixing reactor, the rate of reaction is the same at each instant over the entire surface but varies with time. Therefore the rate at a given time is

$$v = \pm \frac{1}{S}\frac{dN_i}{dt}. \qquad (2)$$

In an ideal plug flow reactor under steady state conditions, the rate of reaction varies along the catalyst bed but remains constant with respect to time for each section of the bed. Therefore for an infinitely thin bed with a surface area dS, at right angles to the axis of the reactor, the rate is

$$v = \pm \frac{1}{t}\frac{dN_i}{dS}. \qquad (3)$$

For a flow reactor, the amount of substance is usually expressed in terms of the number of moles passing through the cross-section of the reactor per unit time: $N' = N/t$. Then Eqn. (3) becomes[5,6]

$$v = \pm \frac{dN_i'}{dS}.$$

The rate equations (1)–(3) can be formulated in terms of other variables. For example, for an ideal plug flow reactor,

$$v = \pm \frac{dN_i}{t\,dS} = \frac{N_0}{t}\frac{d\alpha}{dS} = \frac{N_0}{ts\rho}\frac{d\alpha}{dw} = \frac{N_0}{ts\rho\sigma}\frac{d\alpha}{dl}, \qquad (4)$$

where α is the degree of conversion, N_0 is the number of moles of the starting materials supplied to the reactor during a time t, $\pm N_i = N_0 d\alpha$, s and ρ are respectively the specific surface and the bulk density of the catalyst, σ is the cross-sectional area, and dl and dw are the length and the volume of a catalyst bed with a surface area dS. If the contact time $\tau = w/u$ is employed as a variable for a reaction without a change in the number of molecules, w being the volume of the catalyst bed and u the volume of gas passing through the cross-section of the bed per unit time, Eqn. (4) becomes

$$v = \frac{N_0}{ts\rho}\frac{d\alpha}{dw} = \frac{N_0}{ts\rho u}\frac{d\alpha}{d\tau} = \frac{P_0}{RTs\rho}\frac{d\alpha}{d\tau}, \qquad (5)$$

where $N_0/t = P_0 u/RT$ and P_0 is a constant pressure of the starting material at the inlet to the reactor. An analogous expression for the rate of reaction in terms of the contact time may be written for an ideal-mixing flow reactor:

$$v = \pm \frac{\Delta N_i}{tS} = \frac{N_0\alpha}{ts\rho w} = \frac{P_0}{RTs\rho}\frac{\alpha}{\tau}. \qquad (6)$$

In a reaction involving a change in the number of molecules, the flow rate u becomes a function of the degree of

conversion and the contact time τ in the flow reactor is determined by highly complex formulae, which depend on the form of kinetic equation[7]. Here one can employ as a variable in the rate equation[8] the quantity $\tau' = w/u_0$, where u_0 is the volume of gas passing into the reactor per unit time.

Our definition of the rate of reaction is not unique. Apart from the area of the catalyst surface[5,6,9,10], the rate of reaction may be referred to its unit weight[11], unit volume[12,13], or the length of the bed[14]. It is also possible to refer the rate to the surface area of the active phase or to the number of its active centres if these quantities are known†. The above definitions involve the number of moles of the substance in the numerator and can be readily interconverted on multiplication by appropriate constants. The definition of the rate of reaction in terms of the concentration of the substance[15-17] instead of its amount is not universal and is applicable only to reactions at constant volume, when the concentration varies only due to the reaction and not due to a change in the volume of the system system[10,18,19].

By definition, the rate of reaction v is the rate per unit catalyst surface. However, in the literature the rate of reaction is usually defined as the quantity v' calculated from the experimental data (the observed rate), which refers to a catalyst with a surface area S and the rate of reaction $v = v'/S$ is called the specific rate. We may note that the possible heterogeneity of the surface does not preclude the assignment of the observed rate v' to unit surface, since v characterises the average activity of 1 m^2 of the surface area of the given catalyst. Although in the vast majority of cases the observed rate of reaction on solid catalysts is proportional to their amount[20], it is useful to verify this experimentally. Such a test[21-24] confirms the validity of the definition of the activity of catalysts, since, if the experimental conditions are chosen erroneously, the above proportionality may not in fact obtain. For example, it will not hold for very long contact times in a flow reactor, when a linear relation is obtained between the yield of products per unit time and the rate of supply of the starting material, as has in fact been observed[25,26]. In this case the yield corresponds to equilibrium[27] and is attained on part of the catalyst bed, while the remainder is inactive.

In this review we shall not consider the experimental methods for the determination of the rate of reaction. The problem of the choice of experimental conditions to ensure that the observed rate of reaction characterises the activity of the catalyst has been most fully examined by Boreskov[1,20,28] and also by Dowden and Bridger[29], Germain[3], and de Mourgues[30]. The rate of reaction must be measured under isothermal conditions with the catalyst surface in a steady state and in the absence of an effect of heat and mass transfer processes, i.e. in the kinetic region‡. For a reversible reaction, the rate of the process in one direction only must serve as a measure of activity and not the observed rate, which is equal to the difference between the rates in the forward and reverse directions.

The rate of reaction in the presence of a given catalyst depends on temperature and the concentrations (or pressures) of the reactants and products and also extraneous substances. By virtue of this dependence, the rates for different catalysts can be compared only at the same temperature and pressure and for the same composition of the reaction mixture. Despite this, one sometimes encounters in the literature comparisons where the relevant mixture composition is not stated[31]. The relative activities of a series of catalysts found for the same composition of the reaction mixture may be altered for a different composition owing to varying forms of the kinetic equations valid for these catalysts.

In a gradient-free reactor the rate of reaction is calculated from data for a single experiment by Eqn. (6). It is more difficult to satisfy the conditions of a constant composition of the reaction mixture. It is incorrect to compare the rates of reaction for the same composition and rate of supply of the mixture of starting materials as is sometimes done[32-34]. This is because under such standard conditions the mixture compositions in the system differ owing to the different activities of the catalysts. Identical compositions of the reaction mixture can be achieved by varying the degree of conversion, the rate of supply of the starting materials, the composition of the mixture of starting materials supplied, or the amount of the catalyst as was done by Dzis'ko and coworkers[35-37]. It is also possible to find the kinetic equation for each catalyst and to use it to calculate the rate of reaction for a particular composition of the reaction mixture[38].

In integral reactors it is impossible to measure the rate of reaction but it can be found by the graphical differentiation of the kinetic curve. It can also be calculated from the differential kinetic equation by substituting specified concentrations of the reactants and the rate constant obtained by verifying the integral equation[39]. When the reaction is carried out in an "adsorption layer"[22,31,40,41], the condition of a constant composition of reaction mixture must be replaced by the condition of identical surface concentrations.

A special case of the comparison of catalysts in terms of the rate of reaction for a constant composition of the reaction mixture is the comparison based on the "initial rate", i.e. the rate at the start of the reaction when the concentration of reaction products is zero. Naturally, the concentrations of starting materials in such a comparison must be the same. The initial section of the "degree of conversion–time" (duration of contact) kinetic curve can never be measured directly and therefore the initial rate can only be found by extrapolation. The minimum degree of conversion determined experimentally depends on the accuracy of the analytical method and other conditions. The extrapolation is performed on the assumption that near the zero time the same kinetic law holds as in the region of conversions accessible to experiment.

The method of initial rates is usually employed when the experimental curve has a linear section which on extension passes through the origin of coordinates[24,30,42-45]. A linear section, i.e. a constant reaction rate, is characteristic of the initial part of the kinetic curve described by equations of the Langmuir–Hinshelwood type or by power functions without product inhibition, which in the region of low conversions can be approximated by the equation for zero-order kinetics[46]. Evidently the wider is the region

† The assignment of the rate of reaction to unit surface may be purely formal if the entire surface is not active, which sometimes happens for a catalyst with a large surface area or when the surface area of the active phase of the catalyst is unknown. In some cases the very concept of the catalyst surface is without significance (zeolites). We have adopted the definition of the reaction rate which is most widely used in the Russian literature.

‡ For industrial processes in the diffusion region, a quantitative comparison of the activities of catalysts is impossible; one can only compare the yields of products under specified conditions.

under which a constant reaction rate is observed under these conditions (up to 50% [44] and 60% [45] conversion), the lower is the accuracy needed to demonstrate it. If the accuracy of the analysis does not allow the attainment of the region which may be linear, the use of a tangent to the curve, as in the work of Wade et al. [47], involves large errors. When the reaction kinetics at moderate conversions permit the assumption of a linear section, interpolation formulae and in particular Newton's formula [48,49] may be recommended for extrapolation of the curve.

The application of the method of initial rates to reactions inhibited by products is open to objection (Kiperman [50] and Boudart [51]), since the kinetic equation $v = kC_i^n/C_j^m$, where C_i and C_j are respectively the concentrations of the reactant and the product, is not converted into the equation for zero-order kinetics in the region of low conversions [46]. The slope of the curve described by this equation is infinite at $t = 0$ and extrapolation of the curve is pointless.

There exists the opposite view [52,53] that the initial rate may be determined independently of the form of the kinetic equation, since a power function with inhibition cannot describe the region of low conversions where reaction products are virtually absent. Indeed the rate of reaction in the initial instant cannot be infinite. However, as already stated, a linear section must be always obtained to determine the initial rate. Without this, the absence of product inhibition cannot be assumed, since sometimes it already has an appreciable influence for conversions not exceeding 1% [51].

A flow reactor with a small amount of catalyst, which allows experiments at low conversions and which is called a differential reactor [54-56], is frequently used to determine the initial rate. As in a stirred flow reactor, the rate is calculated by Eqn. (6), i.e. the slight changes in the rate in a thin catalyst bed are neglected. As stated above, the constancy of the rate at low conversions depends not only on the type of reactor and the experimental conditions but also on the type of kinetic equation. Nevertheless, sometimes this problem is not discussed and only the maximum degree of conversion is reported [57]. In determinations of the rate of reaction at moderate and high product concentrations with the aid of the differential reactor [23,56,58,59], the type of kinetic equation does not play any role. In this region the determination of the rate does not involve an extrapolation.

2. COMPARISON OF CATALYST ACTIVITIES IN TERMS OF THE REACTION RATE CONSTANT

We shall formulate in a general form the dependence of the reaction rate on temperature and the concentrations of the reaction mixture components:

$$v = f(T, C_i, C_j).$$

As a rule, for heterogeneous catalytic reactions the multiplier $k(T)$, which depends only on temperature but not on pressure or the composition of the reaction mixture, may be taken outside the function f:

$$v = k(T)\varphi(T, C_i, C_j).$$

In particular, this possibility is illustrated by the review [60] of kinetic equations for catalytic gas-phase reactions investigated in flow reactors. By analogy with the kinetics of simple single-stage reactions, the multiplier $k(T)$ can be conventionally [61] referred to as the reaction rate constant.

For simple reactions, the rate constant is the proportionality coefficient between the rate of reaction and a power function of reactant concentrations only. For heterogeneous catalytic processes, the function φ is usually more complex. Fractional and negative power exponents and variation with product concentration and with temperature are typical. The rate constant in equations with several constants (for example in equations of the Langmuir–Hinshelwood type) is not equal to the rate for unit concentrations of the reaction mixture components. Only in single-term power equations can the rate constant for a multistage process be formally treated like the rate constants for simple reactions.

If in the presence of a series of catalysts a process obeys the same kinetic law, the relative reaction rates will be unchanged for different compositions of the reaction mixtures but equal rate constant ratios. It is then convenient to characterise the activity of the catalyst in terms of the rate constant. However, identical rate laws are usually found only for catalysts of similar types and therefore the method of comparing activities in terms of rate constants is not universal.

The identity of the equation implies the equality of the reaction orders with respect to each substance and for equations with several constants it implies in addition the equality of all the constants which cannot be taken outside the function φ. These are, for example, the adsorption coefficients in Balandin's equation [14], which may differ sharply both for the same catalyst of different temperatures and for catalysts of different chemical types [62,63]. Evidently, because of this difference, the result of comparing catalysts in terms of the rate constants of Balandin's equation, for example as in the work of Balandin and Teteni [62], can be actually directly opposed to the result of comparing them in terms of the rate of reaction for a specified reaction mixture composition. Likewise the constant α in Frost's equation can be used as a measure of activity only if the second constants of the equation β are equal, which has been observed [64,65] for catalysts of the same chemical composition subjected to different preliminary treatments.

Sometimes the constant taken outside the function φ can be represented by a fairly complex expression. For example, in first-order reactions investigated in a pulse microreactor, the adsorption equilibrium constant K and a constant k, which is in fact referred to as the reaction rate constant, may be isolated from this overall constant [66]. In this case the product kK is a measure of the activity [67]. The activation energy is also found from the temperature variation of the logarithm of the product kK. [67]

Usually it is assumed that, when different rate laws apply, it is impossible to compare the activities of catalysts in terms of reaction rate constants because these have different dimensions [61]. However, identical dimensions are necessary but not sufficient. Thus, in the equations $v = k$ and $v = kC_A/C_B$, the rate constants have the same dimensions but their ratio is not equal to the ratio of the reaction rates, which depends on the composition of the reaction mixture.

In the case of different power equations, the catalytic activities are sometimes compared [68] in terms of the rate constants, since these are equal to the rates of reaction at unit concentrations (or pressures). Such a comparison refers of course only to a single composition of the reaction mixture and essentially does not differ in any way from the comparison based on the reaction rates. Similar examples can also be found in the studies of homogeneous reactions [69-71]. Apart from unit concentrations, other

compositions of the reaction mixture are sometimes employed[70,71]. Suppose, for example, that the process takes place in the presence of two catalysts according to the equations

$$v_1 = k_1 C_A,\ v_2 = k_2 C_A C_B.$$

Then

$$\frac{v_1}{v_2} = \frac{k_1 C_A}{k_2 C_A C_B} = \frac{k_1}{k_2 C_B},$$

and the activities of the catalyst at a specified concentration of the substance B may be characterised by the rate constants, having multiplied k_2 or divided k_1 by C_B.

The method of comparing activities analysed above, which arose as a result of the work of a number of investigators, is widely employed. The catalysts are compared in terms of the rate of reaction[24,35-38,42-45,56,58,59] and, when the kinetic equations are identical, in terms of the rate constant[65,72-76]. For example, we shall consider the work of Shcheglov et al.[77], who determined the activities of metals in the Fourth Period in the synthesis of ammonia in a flow-circulation reactor. Because of the identity of the kinetic equations for iron catalysts, their activities were compared in terms of the rate constants. Since the equations for other metals were different, the rates of reaction for similar compositions of the gaseous mixture were adopted as a measure of their activity. In those cases where, by virtue of the large difference between the activities it was impossible to obtain comparable data (the catalysts operated in different temperature ranges), the reaction rates were extrapolated by the Arrhenius equation to temperatures at which measurements are impossible.

However, parameters of the kinetic equation and the Arrhenius equation other than the reaction rate or the rate constant are frequently employed as a measure of activity. We shall consider the most widely used of these methods for characterising activity. As will be shown below, many of these are ambiguous and may lead to serious misunderstanding. As in the discussion of the rate constants, the agreement with the results of comparing catalysts in terms of the reaction rates for the same composition of the reaction mixture will be adopted as a criterion of the reliability of the results which they yield.

3. COMPARISON OF CATALYST ACTIVITIES IN TERMS OF THE DEGREE OF CONVERSION

In studies on catalysts, the degree of conversion α, i.e. the amount of substance which has reacted or the yield of products referred to unit amounts of the catalysts, are frequently employed as a measure of activity. The comparison is carried out at a fixed temperature, initial mixture composition, and time in a static reactor or for a fixed duration of contact in a flow reactor§. Under these conditions and in the absence of side reactions, the degree of conversion is proportional to the yield of products. The wide use of the degree of conversion as a measure of catalytic activity can be explained by the ease of its experimental determination. However, one can point to causes which lead to erroneous conclusions and frequently vitiate the results of such investigations.

§ For reactions involving a change in the number of moles, the duration of contact $\tau = \omega/u$ is not usually calculated and therefore the conversions are compared for the same value of w/u_0, i.e. for different values of τ.

A very common error is the assignment of the degree of conversion to a unit amount of the catalyst[78-82]. α is proportional to the amount of catalyst only for zero-order reactions. The proportionality obtains also in the region of low conversions for reactions whose kinetics can be treated approximately as zero-order under these conditions. In all other cases, a change in the amount of catalyst, for example in its surface area, does not entail a proportional change in the degree of conversion. To demonstrate this, we shall consider a plot of α against time (duration of contact) for reactors of different types. Usually this relation is described by a kinetic curve with saturation[83]. The limit to which α tends is independent of the catalyst and is equal to the equilibrium yield for reversible reactions and to total conversion for irreversible reactions¶.

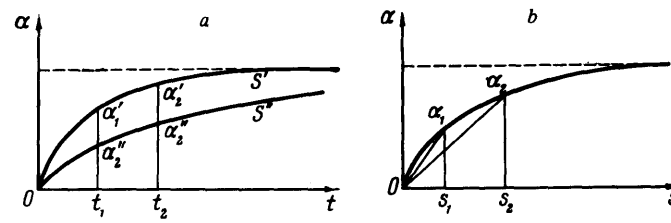


Figure 1. Variation of the degree of conversion with the amount of catalyst: *a*) static reactor; *b*) flow reactor, u_0 = const.

In a static reactor, there is a specific curve relating α to time for each catalyst sample (Fig. 1*a*). For two such curves, the S_1/S_2 ratio is constant and the $(\alpha_1/\alpha_2)_t$ ratio varies with time, since these curves reach the same limit at different rates. Under these conditions for an arbitrarily chosen time, both α/S and the ratio of such quantities for two samples vary along each curve, i.e. $(\alpha_1/S_1)_t \neq (\alpha_2/S_2)_t$. Naturally, the quantity α/S, which depends on the amount of the catalyst, cannot serve as a measure of its activity.

In a flow reactor, it is impossible to determine the variation of α with S or u_0 for a constant contact time, since a change in either of these quantities leads to a change in τ. On the other hand, when S and u_0 are varied simultaneously in such a way that τ remains constant, then α does not vary either. Therefore it is possible to investigate the variation of α with S or u_0 only keeping u_0 or S constant but not τ. The variation of α with $1/u_0$ for two samples of the same catalyst has the same form as the $\alpha - t$ plot for a static reactor (Fig. 1*a*). If the amount of catalyst is varied for a constant rate of supply (of the reactants), the curve shown in Fig. 1*b* is obtained. It is readily seen that in both cases α increases more slowly than S despite the fact that the contact time also increases. Two different catalysts are usually compared for a constant u_0 and volume of the bed. The degree of conversion obtained in such experiments qualitatively characterises the activities of the catalyst volumes employed but it cannot be adjusted for any other volume or any other surface area.

¶ The limiting non-equilibrium yield sometimes observed may be due to the inhibition of the reaction by its products.

In a gradient-free reactor the degree of conversion is proportional to the observed reaction rate and can be referred to a unit amount of the catalyst. However, it would be erroneous to assume that the degrees of conversion obtained for constant rates of supply and compositions of the mixture at the inlet to the reactor may serve as a reliable characteristic of the activity. An increase in the amount of catalyst under these conditions leads to an increase of the observed reaction rate and degree of conversion, i.e. to a change in the composition of the reaction mixture. This in turn entails a decrease of the reaction rate and causes a breakdown of the proportionality between the observed rate and the degree of conversion, on the one hand, and the amount of catalyst, on the other. Therefore comparison of catalysts in terms of the values of α/S is equivalent to the comparison of the reaction rates for different compositions of the reaction mixture.

One can point to examples of unjustified conclusions arrived at by referring α to a unit amount of the catalyst. Tetenyi et al.[84] used a flow reactor to study the activity in three reactions of nickel obtained by different procedures. The conclusion that it had different specific activities was based on a comparison of the amount of unreacted starting material referred to unit catalyst surface. The specific surface of the catalysts varied from 0.5 to 39.3 $m^2 g^{-1}$, i.e. by a factor of 80. Since zero order kinetics were not observed for the reactions investigated, the change in the amount of reactant for identical catalyst samples should be less than the change in surface area, if a constant specific activity is postulated. Indeed the maximum difference between the amounts of starting materials which have reacted is a factor of 12. After referring the conversion to unit surface, catalysts with larger surface areas proved to be "less active". This result provides no information about the constancy or variability of the specific activity of nickel obtained in different ways.

Specific surfaces and activities of $Ni-Al_2O_3$ catalysts according to Swift et al.[85]

Catalyst	Ni, %	$S_{sp\ Ni}$, m^2 g cat.	Activity, % conversion	
			per g of cat.	per m^2 of Ni
$Ni-\eta-Al_2O_3$	6.48	0.58	16.0	27.6
$Ni-\gamma-Al_2O_3$	6.00	1.24	25.0	20.2

Similar objections can be made to a comparison of the activities of two catalysts with the same contents of nickel deposited on η- and γ-Al_2O_3 in the dehydrogenation of cyclohexane[85]. The activity is characterised by the degree of conversion of cyclohexane per gram of catalyst at a constant flow rate through the reactor. The Table shows that the surface area of the active phase in the $Ni-\gamma-Al_2O_3$ catalyst was twice as great, while the degree of conversion of cyclohexane in its presence was higher by a factor of 1.5. After referring α to unit surface of nickel, this catalyst proved to be "less active". To account for the different effects of carriers, the authors investigated their structures and put forward a number of hypotheses. However, the method of comparison which they chose does not allow a decision as to whether there really is a difference between the specific activities of the catalysts investigated.

Unfortunately similar misunderstandings are still encountered fairly frequently on studies of heterogeneous catalysis[86-89].

The lack of proportionality between the degree of conversion and the amount of catalyst is a serious obstacle to the employment of α as a measure of catalytic activity. Naturally, one can point to certain specific problems concerning one particular catalyst, where it is sufficient to know the degree of conversion without referring it to unit catalyst surface. For example, these include tests for the reproducibility of the activity and for the absence of diffusion-dependent inhibition[89], the choice of regeneration conditions[90], the study of the effect of poisons[91] or extraneous substances[92,93], etc. A qualitative comparison of the change in product yield during the experiment and a physical property of the catalyst[94,95] may be accepted, provided that the specific surface remains unaltered in the experiment. However, none of these cases have a direct bearing on the problem of comparing the activities of different catalysts.

As a result of the absence of a proportionality between the degree of conversion and the amount of catalyst, the experimentally determined value of α characterises only the activity of the amount of catalyst employed in the experiment. In a static reactor, it is possible to compare the degrees of conversion obtained during the same period in the presence of different catalysts provided that samples are employed for which the quantitative measure of activity is the same. In a flow reactor samples are also sometimes chosen for which the surface area[96,97], the number of elementary zeolite cells[98], etc. are the same; the comparison is performed at a constant rate of supply. However, owing to differences between the volumes of the catalysts, the comparison in this case involves different contact times.

We shall now point to another cause of the unreliability of characterising catalytic activity with the aid of α determined using an integral reactor. We shall suppose that the amount of catalyst need not be taken into account, since the degrees of conversion during equal periods have been determined for samples with the same quantitative measures of activity, for example the surface area of the active phase. Under this condition, it is also possible to obtain erroneous results, since the ratio of the degrees of conversion is not equal to the ratio of the reaction rates for the same composition of the reaction mixture.

Suppose that in Fig. 2*a* curves I and II refer to two different catalysts taken in identical amounts and catalysing a single process at the same rate. The ratio α_1/α_2, i.e. the ratio of the tangents of the angles ψ_1 and ψ_2, differs appreciably in magnitude from the ratio of the tangents of the angles ψ_3 and ψ_4 defining the slopes of the curves for the mixture composition corresponding to α_1:

$$\left(\frac{\alpha_2}{\alpha_1}\right)_t = \frac{\tan\psi_2}{\tan\psi_1} < \frac{\tan\psi_4}{\tan\psi_3} = \left(\frac{v_2}{v_1}\right)_{\alpha_1},$$

because $\psi_4 > \psi_2$ and $\psi_3 < \psi_1$. Thus the degree of conversion cannot serve as a quantitative characteristic of activity. On the other hand, if the kinetic equations for two catalysts are different, comparison in terms of α can also yield a qualitatively incorrect result. In Fig. 2*b*, α for the upper curve is larger, while the initial rate is also higher but subsequently becomes lower than for the lower curve. If the $\alpha - t$ kinetic curves for two catalysts intersect, the same pattern as in Fig. 2*b* is repeated up to the point of intersection. At the point of intersection the degree of conversion is the same but the rates of reaction are different. In a comparison of the catalysts in terms

of α, the form of the kinetic equation is usually unknown. Therefore there is always a risk that an incorrect result will be obtained, since the equations may be different not only for catalysts of similar composition but even for the same catalyst when the composition of the reaction mixture is changed, as was observed, for example, by Kiperman and coworkers[99,100].

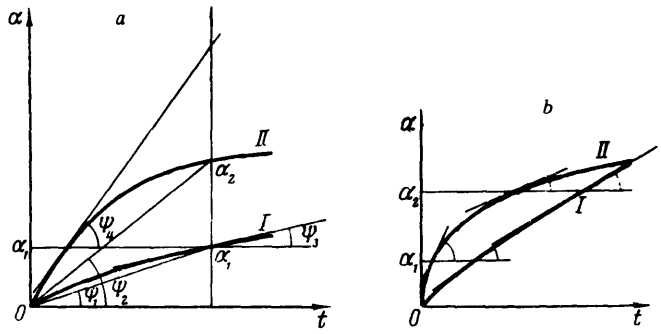


Figure 2. Comparison of the activities of two catalysts in terms of the degree of conversion and reaction rate: *a*) $\alpha_2/\alpha_1 < (v_2/v_1)_{\alpha_1}$; *b*) $v_2 > v_1$ for $\alpha = \alpha_1$ and $v_2 < v_1$ for $\alpha = \alpha_2$.

Thus the method of comparing catalyst activities in terms of degrees of conversion or product yields must be treated with considerable caution. The errors associated with the application of this method are still being encountered in studies on heterogeneous catalysis, although the risk of such errors has been pointed out repeatedly[75,101,102]. Dixon and Webb have reported[103] that, in contrast to heterogeneous catalysis, in the field of enzymatic catalysis comparison of the changes in concentration over a specified period has been completely abandoned in recent years and the method of initial rates is mainly employed.

4. COMPARISON OF THE ACTIVITIES OF CATALYSTS IN TERMS OF THE TIME REQUIRED FOR THE ATTAINMENT OF A GIVEN DEGREE OF CONVERSION

The possibility of a quantitative comparison of catalytic activities in integral reactors without determining the type of kinetic equation, which is provided by the time required for the attainment of a specified degree of conversion as a measure of activity[102], is extremely attractive. It is possible to show[104] that, for $2\alpha - t$ curves described by the same equation, the rate constant ratio is equal to the reciprocal of the ratio of the times required for the attainment of a specified degree of conversion of the starting material when its initial concentrations are the same:

$$\frac{k'}{k''} = \frac{t''_\alpha}{t'_\alpha}. \qquad (7)$$

Therefore the quantity $1/t_\alpha$ is referred to a unit amount of the catalysts[22,105] and is used as a quantitative characteristic of activity. It is evident from Eqn. (7) that the ratio of the quantities t_α for two catalysts is independent of the degree of conversion chosen arbitrarily for comparison in the range of mixture compositions where a single kinetic equation holds (Fig. 3*a*).

For a flow reactor, the contact time w/u_0 [106,107] or the proportional quantities $1/u_0$, G/u_0, [102] Su_0, or G^*/u_0 [108], where G and G^* are the weights of the catalyst and the active phase respectively, etc., are employed instead of time.† Depending on the factor used, different activities are obtained. For the same degree of conversion, the values of $1/u_0$ are proportional to the rate constants corresponding to the total amount of catalyst taken for the reaction, the values of S/u_0 are proportional to the rate constants referred to unit catalyst surface, etc.

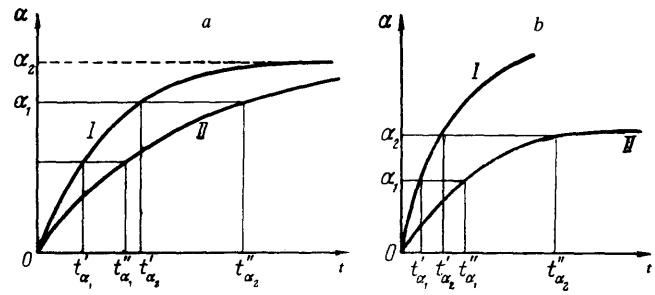


Figure 3. Time required for the attainment of a specified degree of conversion: *a*) $t'_{\alpha_1}/t''_{\alpha_1} = t'_{\alpha_2}/t''_{\alpha_2} = \text{const.}$; *b*) $t'_{\alpha_1}/t''_{\alpha_1} \neq t'_{\alpha_2}/t''_{\alpha_2}$.

Comparison of catalysts in terms of the time required to attain the same degree of conversion is restricted by the same condition as the comparison in terms of rate constants—it is permissible only when the kinetic equations are identical. We may recall that, for an equation with several constants, identity implies the equality of all the constants other than the rate constant. However, if the equation is known, the rate constant is also known and there is no need to replace it by t_α. It is possible to verify the identity of the kinetic equations by a graphical method without determining their form. For this purpose, it is sufficient to superimpose the kinetic curves (Fig. 3*a*) by altering the scale along the abscissa. The constancy of the ratios of t_α for different α can also serve to confirm the identity of the equations. Without such a test, there is always a risk that the equations are different and the method of comparing the activities is inapplicable.

An impression might be created that, regardless of the type of kinetic equation, a higher activity is always associated with a shorter time to attain a specified percentage conversion. That this view is erroneous can be demonstrated with the aid of Fig. 2*b* already examined: t_α for the upper curve is smaller, while the rate of reaction (the slope of the curve) is initially higher and then lower than for the lower curve. If the $\alpha - t$ curves intersect, then at the point of intersection the rates are different while t_α is the same. Thus for different kinetic

† w/u_0 is more correctly called the reciprocal of the space velocity.

equations, comparison of catalysts in terms of the values of $1/t_\alpha$ may be incorrect.

For a reversible reaction investigated at the same temperature in the presence of different catalysts, the same degree of conversion implies also the same degree of deviation from equilibrium and therefore the effect of the reverse reaction on the observed rate of the process will also be the same. The derivation of Eqn. (7), obtained for an irreversible reaction[104], can be extended to this case. For this purpose, it is convenient to employ the criterion of the effect of the reverse reaction γ proposed by Kiperman and Gadzhi-Kasumov[109]. The observed rate of the reverse reaction is

$$v = \vec{k}\vec{\varphi}(C_i)\gamma,$$

where $\vec{k}$ and $\vec{\varphi}(C_i)$ are respectively the rate constant and a function of the concentrations of the reaction mixture components for the forward reaction; γ depends on the degree of departure from equilibrium y. The latter is determined as a fraction of the yield of reaction products relative to the equilibrium value. For the same degree of conversion and an unchanged equilibrium yield, the values of y and γ will also be the same, i.e. Eqn. (7) will hold for a reversible reaction occurring in the presence of two catalysts according to an identical kinetic law.

If the $\alpha - t$ curves have been obtained for the same catalyst at different temperatures, the temperature variation of $1/t_\alpha$ is used to determine the apparent activation energy[41,110,111]. This is valid either when the equilibrium yield in the temperature range investigated is almost constant or for large departures from equilibrium. In the same cases, when the equilibrium yield varies with temperature, an identical degree of conversion is associated with different degrees of deviation from equilibrium and consequently with different values of γ. Then the ratio t'_α/t''_α at two temperatures depends on the value of α (Fig. 3*b*) and cannot be used to calculate the activation energy. The constancy of the activation energy for different α can indicate both[111] the absence of an effect by the reverse reaction and the identity of the kinetic equation in the given temperature range.

5. COMPARISON OF THE ACTIVITIES OF CATALYSTS IN TERMS OF THE TEMPERATURE AT WHICH THE DEGREE OF CONVERSION OR THE REACTION RATE HAS A SPECIFIED VALUE

We shall consider in turn the different variants of the methods for comparing catalysts in terms of the reciprocals of the temperatures at which a particular degree of conversion or reaction rate is attained. The temperature of the onset of reaction[110] is the most indeterminate characteristic of the activity. The experimentally observed onset of reaction depends on the sensitivity of the analytical method and, since it is a quantity lying at the limit of sensitivity, its determination is inaccurate. The possible errors are compounded by the fact that in the region of low conversions a small change in α usually corresponds to a considerable change in temperature. Comparison of the temperatures corresponding to complete conversion is open to similar objections[112].

Therefore it is best to compare the temperatures T_α at which the same degree of conversion is attained in a specified time (the contact time) [113-120] for constant initial concentrations. However, this method has a number of disadvantages associated with the indeterminacy of the degree of conversion as a measure of activity. T_α depends on the amount of catalyst and it is impossible to take into account this relation. Moreover, for integral reactors T_α is not always the temperature at which the catalysts have the same activity because, owing to different forms of the kinetic equation, the same value of α for a constant τ may correspond to different reaction rates.

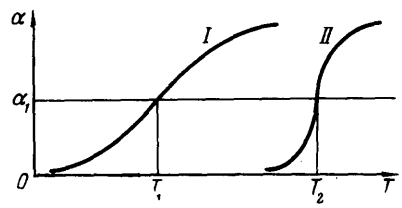


Figure 4. Temperature variation of the degree of conversion.

The variation of α with T for a constant τ is represented by S-shaped curves (Fig. 4, curve *I*)[113,117-120], which are displaced when the rate of supply of the starting material or the amount of catalyst is altered[121]. Takeuchi et al.[120] observed such a sharp increase of α at a specified temperature (curve II) that this temperature was no longer dependent on the amount of catalyst. Therefore they regarded it as a specific characteristic of the catalyst, although the phenomenon might have been associated with the non-isothermal experimental conditions.

In work with reactors allowing the determination of the rate of reaction in a single experiment, the activity is characterised by the temperature T_v, at which the rate of the reaction has a specified value[30,122-125]. Naturally, the comparison must be made for a constant reaction mixture composition. An attempt to employ this method was made by Rubanik et al.[123] in a stirred flow reactor. Deciding against extrapolation of the reaction rate, they adopted as a measure of activity the "temperature at which the same reaction rate, referred to unit catalyst surface, is attained" for constant concentrations of the reactants in the system. However, in fact this characteristic of the activity was not obtained. The surface areas of the catalysts differed at most by a factor of 15. The experiments were performed at a constant volume of the catalyst bed, flow rate, and composition of the gas mixture at the inlet to the reactor. Under these conditions, an identical observed reaction rate v' would imply a constant concentration of all the substances in the system. However, the temperatures were not compared for the same value of v' but for the same value of v'/S, which corresponded to different values of v' and consequently to different compositions of the reaction mixture.

It is possible to avoid the need to allow for surface areas, using catalyst samples for which these areas are the same. It is also possible to achieve the same mixture composition in the reactor for identical values of v'/S by altering the flow rate or the composition of the mixture supplied. The above difficulty of allowing for the amount of catalyst is obviated when the rate of reaction is determined in a differential flow reactor. A constant mixture composition at the inlet and a sufficiently low degree of

of conversion at all temperatures ensure an approximately identical composition of the reaction mixture. This permits a comparison of the temperatures at which the values of $v = v'/S$ are identical.

However, even in the most rigorous variant the reciprocal of the temperature cannot serve as a quantitative criterion of activity in place of the reaction rate, since these quantities are not proportional. In order to justify the use of T_v as a qualitative characteristic of activity, we shall consider the temperature variation of the reaction rate. If for a particular process the same single-term kinetic equation of a power function type holds over a range of temperatures and the Arrhenius law is valid, then

$$v = k\varphi(C_i) = k_0 e^{-E/RT}\varphi(C_i). \quad (8)$$

In this case the temperature variation of the rate constant for a positive activation energy is represented by a rising S-shaped curve. Evidently for a constant composition of the reaction mixture, the $v-T$ plot is also S-shaped. Its specific form is determined by the relative values of k_0, E, and the function φ for specified concentrations. In practice such curves can be readily obtained in a differential flow reactor.

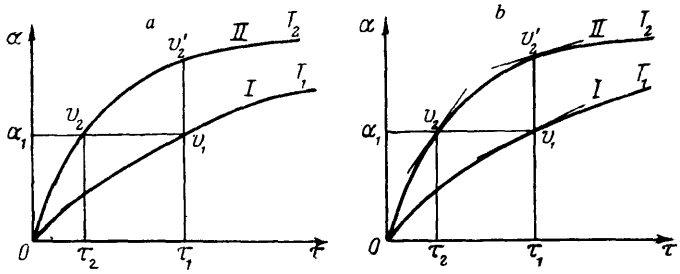


Figure 5. Temperature variation of the reaction rate: *a*) stirred flow reactor; *b*) flow reactor.

In a gradient-free reactor, for a constant contact time and mixture composition at the inlet, the rate of reaction calculated by Eqn. (6) can also only increase with temperature. Suppose that, when the temperature is raised from T_1 to T_2 and α = const., i.e. $\varphi(C_i)$ = const., the rate of reaction increases from v_1 to v_2 (Fig. 5*a*) and the entire curve II lies above curve I, since by our hypothesis they are described by a single equation and cannot intersect. We then increase t_2 to $t_2' = t_1$. The reaction rate v_2' will be higher than v_1, since $\alpha_2' > \alpha_1$.

In contrast to gradient-free reactors, in integral reactors for constant initial concentrations and times (durations of contact) the reaction rate can both increase with temperature and pass through a maximum. Fig. 5*b* shows that $\alpha_2' > \alpha_1$ but $v_2' < v_1$.

Hitherto we have assumed that a single-term power equation holds over a range of temperatures and the activation energy is positive. However, the kinetic equation can contain, apart from the rate constant for the forward reaction, also other constants which depend on temperature (the adsorption coefficients and the rate constants for elementary stages or the reverse reaction). Then both the degree of conversion and the rate of reaction in any reactor are bound to increase with temperature.

Reactions are known with a maximum rate (hydrogenation of olefins[126] and benzene[127]) and degree of conversion (synthesis of ammonia[128]) with respect to temperature. Therefore, for a comparison of catalysts both in terms of T_v and T_α, it is necessary to investigate the variation of v or α with T over a wide temperature range.

The $v-T$ curves for different catalysts may intersect. It has been frequently pointed out[129-131] that temperature is unsuitable as a criterion of activity for different activation energies, since catalysts may be classified as identical or different depending on the rate of reaction chosen arbitrarily for the comparison. There is a risk of arriving at an incorrect result when each catalyst is characterised by a single value of T_v. But if one considers two intersecting curves, the dependence of the result of the comparison on an arbitrarily chosen value of v cannot serve as evidence against the use of T_v as a criterion of activity. The temperature at which the reaction rates are compared is after all chosen just as arbitrarily. At the same time the comparison in terms of T_v yields the same activity series as the comparison in terms of reaction rates at the same temperature, provided that both temperatures and both reaction rates lie on one side of the point of intersection (Fig. 6). Indeed $v_1 > v_2$ and $T_1 < T_2$ but $v_1^* < v_2^*$ and $T_1^* > T_2^*$. When several curves intersect, a more complex pattern may be obtained. Therefore T_v should not be used for the comparison of catalysts with similar activities, particularly since T_v is a less sensitive characteristic than v because of the exponential relation between v and T.

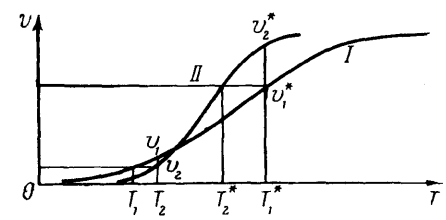


Figure 6. Comparison of the activities of two catalysts in terms of T_v and v.

Thus comparison of catalysts in terms of T_v may yield the correct series of their activities but not their relative values. At the same time the reliability of the results of the comparison in terms of T_α is extremely doubtful, particularly if the differences between the activities are not very great[116] or are absent[132], the $\alpha-T$ curves are not quoted, and there are no data concerning the identity of the kinetic equations.

The use of T_v as a measure of activity is quite justified when a direct comparison of the rates of reaction is impossible because of the different temperature ranges in which the catalysts were used[30]. De Mourgues[30] has mentioned that a comparison of the T_v "yields less quantitative information but is more valid, since it is based on actual and not extrapolated results". This view is shared also by other investigators[125,131,133], although essentially temperature as a measure of activity has no advantages over reaction rates. There may be doubts about the actual values of the extrapolated rate ratios but not about the order of activities based on them.

6. COMPARISON OF THE ACTIVITIES OF CATALYSTS IN TERMS OF ACTIVATION ENERGY

In order to correlate the activities of catalysts with their physical properties, it is extremely desirable to have a characteristic of the activity which depends on the least possible number of process parameters. We shall examine the possibility of using as a kinetic correlation parameter the activation energy—a quantity which is not only independent of the amount of catalyst and the concentrations of the reactants and products but is also constant over a range of temperatures. Although the catalyst reduces the activation energy for the reaction, a reduced value of E cannot be regarded as evidence of higher activity. This method of characterising activity is restricted by a number of conditions. In the first place these are the conditions analogous to those restricting the use of rate constants: (1) if the kinetic equation involves several constants varying with temperature, the activation energy found from the logarithms of the rate constant does not fully reflect the temperature variation of the rate of reaction[1] and cannot therefore replace it as a measure of activity; (2) if different equations hold for different catalysts, then, as shown above, the rate constants cannot serve as a measure of activity and therefore the activation energy is also unsuitable for the purpose of comparison.

Comparison of catalysts in terms of activation energies is possible only when the kinetic equations, with a single temperature-dependent constant, are identical. Eqn. (8) shows that, by virtue of the exponential relation between v and E, the activation energy as well as temperature can serve only as a qualitative characteristic of activity and is less sensitive than the reaction rate.

The last limitation of the method of comparing catalysts in terms of activation energies, which has been frequently pointed out[101,131,134,135], is the necessity to take into account the pre-exponential factor k_0.

Its variability for different catalysts leads to an ambiguous relation between k and E. Indeed, for the same E and different k_0, the activities of catalysts expressed by the rate constants will be different at all temperatures. When E and k_0 vary in parallel (the compensation effect), the linear Arrhenius plots should intersect. Then the activation energy, which is constant over the entire range of temperatures, cannot reflect the reversal of the relative activities at the point of intersection (Fig. 7).

The Arrhenius plot always shows whether the straight lines intersect in the temperature range investigated and whether they can intersect beyond it. The rate constants must then of course be referred to a unit amount of the catalyst.

Thus, for a comparison of catalysts with the aid of activation energies, it is necessary to analyse the relative positions of the linear Arrhenius plots, just as for a comparison in terms of T_V it is necessary to examine the curves relating v to T. Bearing in mind all possible cases of a simultaneous variation of E and k_0 for two catalysts discussed in the literature[136,137], we conclude that the activation energy cannot characterise the activity for parallel or intersecting straight lines when the point of intersection lies in the temperature range investigated or to the right of it.

Thus taking into account the limitations discussed above, the activation energy may be used as a qualitative characteristic of activity. But for the calculation of E, it is necessary to determine initially the rate constant or the rate of reaction over a range of temperatures, which makes it possible to characterise the activity incomparably more accurately without resorting to the activation energy.

The activation energy is employed as a measure of activity mainly in studies dealing with the elucidation of the role of the electronic factor in catalysis. Examples may be found in the reviews of Baker and Jenkins[138] and Schwab[139,140]. When additives are introduced into catalysts (semiconductors or metals deposited on semiconductors), the parallel changes in their activity and electrical properties are compared. The activation energy is determined as a rule from the temperature variation of the initial rate. For equations with a single constant which varies with temperature,

$$\left(\frac{\partial \ln v}{\partial T}\right)_{C_i} = \frac{d \ln k}{d},$$

i.e. when the composition of the gas phase remains unchanged, the apparent activation energy may be determined from the rate of reaction[141,142]. Then, in order to compare the catalysts in terms of the activation energies, account must be taken, instead of k_0, of the variation of v_0—the rate of reaction extrapolated to an infinite temperature. Since for a single-term power equation

$$\lg v = \lg k - \sum n_i \lg C_i,$$

the difference between the $\lg v_0$ is equal to the difference between the $\lg k_0$ when the equations for two catalysts are identical, and the $\lg v - 1/T$ and $\lg k - 1/T$ straight lines intersect at the same temperature.

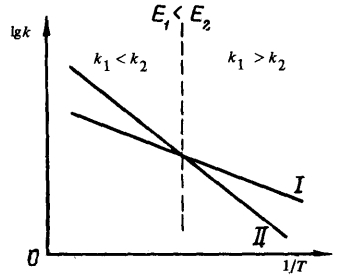


Figure 7. Activation energy as a measure of the activity when linear Arrhenius plots intersect.

When the reaction order changes over a range of temperatures, the activation energies calculated from the rates of reaction[143-145] as well as from the rate constants lose their significance. Therefore it is not surprising that the values of E found for the hydrogenation of benzene on the $Ni-Al_2O_3$ catalyst from the initial rates under the conditions of a variable reaction order and from the rate constants in an equation of the Langmuir–Hinshelwood type are markedly different (16 and 28 kcal mole^{-1}) [143]. There is no reason to regard either of the above quantities as the activation energy for the reaction.

Comparison of catalysts in terms of activation energies is usually not reliable, since it is made without allowance for all the above conditions. The retention of the identical form of the kinetic equation on introduction of an additive into the semiconductor has not been verified[146,147] although the mechanism and processes of semiconductor catalysts may alter under the influence of very small amounts of

impurities. For example, according to the data of Bielanski et al.[68], when 0.1 at. % of iron is added to nickel oxide, the overall order of the CO oxidation reaction changes from first to zero. The change in E is discussed without taking into account the possible change in the pre-exponential factor[146]. Schwab has reported in some papers[148,149] that there is a linear relation between E and k_0 and the temperature corresponding to equal rates for all the catalysts lies above the working range. On the other hand, in other studies this has not been verified[147] or confirmed[148], but E is nevertheless regarded as a characteristic of the activity.

It is clear from the foregoing that it is more desirable to estimate the catalytic activity with the aid of rate constants or reaction rates and the activation energy should be correlated as an energy characteristic of the surface with the activation energy for electrical conduction, electron work function, etc.[74,105]. In correlations of this kind, the variation of k_0 does not play any role, while the remaining limitations remain in force. Teichner[150] concluded that the correlation of the activity with the catalyst properties is best based on the true and not the apparent activation energy, since the change in E on introduction of an additive may be caused by a change in surface coverage and reaction order. The constancy of the reaction order is of course a necessary condition for the comparison of the values of E in the presence of different catalysts but this need not be a zero order and the use of the true activation energy is not necessary.

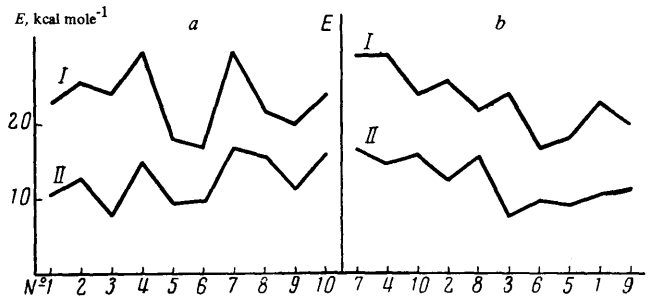


Figure 8. Variation of the activation energy for the dehydrogenation of cyclohexane (curve *1*) and isopropyl alcohol (curve *2*) with the number of the catalyst: a) according to the data of Firth and Holland[152]: *b*) when the order of the catalysts is altered.

The correlation should not be based on the variation with the number of the catalyst arbitrarily assigned by the investigator[84,151,153]. For example, the parallel variation of the activation energies for the dehydrogenation of isopropyl alcohol and cyclohexane in the presence of a series of nickel specimens prepared in different ways[151] can be readily transformed into the opposite variation when the numbers of the catalysts are transposed (Fig. 8).

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Thus we have seen that catalytic activity should be characterised in terms of the reaction rates under rigorously defined conditions. The use for this purpose of other quantities is possible if it is known that the result of their comparison agrees quantitatively or at least qualitatively with the result of a comparison of the rates of reaction at the same temperature and for the same concentrations of all the substances which affect the rate. When this criterion is fulfilled, activity may be characterised, apart from the parameters of the kinetic equation and the Arrhenius equation discussed above, by any other quantity, for example, the rate of evolution of heat when the reaction is performed in a microcalorimeter[152].

Recently attempts have been made to employ correlation analysis for a comparison of the activities of catalysts with their properties. The reaction parameter is the linear relation between free energies yields a general characteristic of the activity of the catalyst for a series of compounds undergoing the same reaction[153,154]. As for the rate constant, its use is restricted by the condition that the kinetic equations must be identical.

We must emphasise that for an accurate expression of catalytic activity, it is sufficient to determine the reaction rates and the knowledge of the mechanism and kinetics of the process does not by itself play a role. Another problem is that in integral reactors the study of kinetics is necessary for the calculation of the reaction rates, while in gradient-free reactors the kinetic equation can be conveniently used to determine the rate of reaction for a specified composition of the reaction mixture. Thus the obligatory need to study the kinetics in order to estimate catalytic activity, which is frequently pointed out[101,137], is valid only for integral reactors.

The aim of a study of catalytic activity can be either practical (the choice of the optimum catalyst and the optimisation of the process) or theoretical (the elucidation of the relation with composition, structure, and physical properties of the catalyst)[3]. In both cases a comparison of the reaction rates is necessary but not sufficient. For the first aim to be achieved, it is in addition important to know the activity of each catalyst under its optimum conditions[155-157,159] and then to decide for which of them the process is more economical.

Attempts are usually made to achieve the second aim by correlating the activity with the properties of the catalyst as a solid. The variation of the reaction rate with concentrations and temperature makes it impossible to characterise the activity also as a property of the solid. "One can speak rigorously only of the catalytic activity characteristic of the entire system, including the catalyst and the reaction mixture"[1]. Therefore the activity should be characterised by a set of reaction rates over a wide range of concentrations and temperatures. Comparison of the activities under one particular set of conditions is insufficient for correlations with the properties of the catalyst as a solid.

In theoretical studies on catalysts, de Mourgues[30] recommends that the simplest reactions be chosen as models. For complex processes, i.e. when several reactions take place simultaneously, the rate of the main reaction or the overall rate of the process may be adopted as a measure of activity.

In conclusion we may note that in the present review the authors endeavoured to describe the present state of the problem and not its history. The review does not pretend to be complete and the choice of specific examples, the aim of which was to make them typical, may inevitably prove to be arbitrary.

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Zelinskii Institute of Organic Chemistry, USSR Academy of Sciences, Moscow