PROBLEMS AND CHALLENGES ABOUT ACCELERATED TESTING OF THE CATALYTIC ACTIVITY OF CATALYSTS

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1. Introduction

Catalysis, as one of the most frequently observed natural phenomena, is the basic form of chemical reactions proceeding at a high rate in nature as well as in different fields of practical activities.

Being a fundamental science catalysis is developing at the interface of chemistry, physics, biology, and mathematics; this is a circumstance, which determines the great complexity and value of the investigations as well as the difficulty in interpretation of the obtained results.

Catalysis is the most powerful method of controlling and directing chemical reactions. Competent international forecasts place catalysis among the most promising fields of basic research. The successes of basic research in the field of catalysis have a direct effect on solving many fundamental technological, environmental and social problems that face humanity. These include efficient utilisation of raw materials and formation of new sources of raw materials, invention of new materials and substances with pre-programmed properties, development of efficient systems for environmental protection, mastering of new sources of energy and improvement of existing ones, and development of new processes and technologies in chemistry and biology. Industrially developed countries take the importance of catalysis into account. Catalytic processes form the fundamentals of modern chemical and petrochemical industries. Over 70% of the processes in these industries are catalytic, while for the newly introduced ones this percentage is over 90. In the highly developed industrial countries catalytic processes create about 20% of the Gross Domestic Product. Catalysis is one of the top priority issues of chemical science and many countries have founded specialised institutes and laboratories for basic research and applied studies in the field of catalysis [1].

Effective application of the existing catalysts and development of new types needs precise and fast information about their catalytic properties. The determination of catalytic activity, selectivity and lifetime of an industrial catalyst for a certain catalytic process is a difficult, expensive and time-consuming task [2 – 8].

In this paper we shall discuss the most common approaches and problems one could encounter during the testing of catalytic properties of the industrial catalysts.

2. Industrial Catalysts

Catalysts belong to the group of so called performance chemicals. In general, they have complex composition (often supported on carriers or dissolved in solvents) and are added to the reaction mixture to enhance processing of other chemicals. In most of the cases, industrial catalysts contain three groups of components: catalytically active materials, catalyst supports, and promoters. Short information about industrial catalysts is given below [9 – 13].

2.1. CATALYTICALLY ACTIVE MATERIALS

A great number of materials of different nature exhibit a certain catalytic activity in one or more catalytic reactions. However, only few of them are suitable for preparation of industrial catalysts. There is a substantial difference between catalytically active materials and industrial catalysts. The catalytically active material should be regarded as precursor of an industrial catalyst that has to undergo many transformations and treatments to become a real industrial catalyst. Catalytically active materials usually possess appropriate catalytic properties (activity and selectivity) but still do not have the complex of properties, which are required for industrial catalysts.

The effective industrial catalysts are products, which possess a special complex of different properties and should be selected using the following criteria: (i) high catalytic activity; (ii) high selectivity; (iii) proper pore structure; (iv) long lifetime; (v) high resistance to deactivation and catalytic poisons; (vi) easy regeneration; (vii) low operation and light-off temperature; (viii) high thermal stability; (ix) high thermal conductivity; (x) high mechanical strength; (xi) high resistance to attrition; (xii) low price.

It is impossible however, to prepare an industrial catalyst that meets strictly all above-mentioned requirements. In order to obtain the best possible performance in the industrial units it is necessary to make a compromise for the extent at which all necessary requirements are satisfied.

The typical groups of catalytically active materials involve metals, multimetallic clusters, oxides, sulphides, acids and bases, chlorides, carbides, nitrides, borides, silicides, phosphides, molten salts, anchored homogeneous catalysts. As mentioned before, the most suitable individual catalytically active material has to be selected for every process.

2.2. CATALYST SUPPORTS

Most of the industrial heterogeneous catalyst compositions contain catalyst supports. In general, it is accepted that the catalyst support has either a low catalytic activity or is totally inactive for most of the catalytic reactions for which supported catalysts are used.

The carriers are being selected according to the following major criteria: (i) low catalytic activity; (ii) large surface area and ability to stabilise supported metal particles; (iii) optimum porosity and pore size distribution; (iv) chemical properties of the surface; (v) resistance to reaction media; (vi) very good mechanical properties; (vii) very good thermal stability and resistance to sintering; (viii) stable behaviour during the regeneration process; (ix) low price.

In view of their surface chemical properties the supports can be classified in four major groups: basic supports (MgO, CaO, BaO), acidic supports (γ-Al_2O_3, SiO_2, Al_2O_3/SiO_2, zeolites), neutral supports ($MgAl_2O_4$, $MgCr_2O_4$, $ZrCrO_4$, $ZnAl_2O_4$), and amphoteric supports (α-Al_2O_3, TiO_2, CeO_2, ZrO_2).

2.3. CATALYST PROMOTERS

Catalyst promoters are elements or substances, which are added in small quantities and change substantially different properties of the catalysts. Their action is always strictly individual.

3. Aims of Catalytic Activity Tests

3.1. QUALITY CONTROL TESTS

This is the simplest case. Industrial catalysts are produced under standard and well-controlled reproducible conditions and small variations around the standard performance can be expected. The kinetics of the reaction is always known and adequate kinetic model has been built. In this case the typical test is done by feeding the reactor with several constant feed composition and difference in catalyst activity can be expressed in terms of different degree of conversion or reaction rate at constant temperature and flow rate. Catalyst producers and catalyst users for checking of the standard activity can use the results of this test and selectivity of tested catalyst.

The quality control tests are performed in laboratory equipment.

3.2. IMPROVEMENT OF THE CATALYST FOR AN EXISTING PROCESS

When a catalyst with well-known performance is used for a long time the quality control test is sufficient for its properties characterisation.

Introduction of the new catalyst in the existing industrial unit needs much more diverse information about: (i) Reaction kinetics and kinetic model; (ii) Catalytic activity and selectivity of the catalyst; (iii) Regimes for the catalyst pre-treatment; (iv) Kinetics of catalyst deactivation; (v) Regimes for catalyst regeneration; (vi) Lifetime of the catalyst; (vii) Safety transition regimes in cases of industrial accident. Reliable methods for every issue mentioned before should be available.

In connection with above mentioned three important limitations exist:

(i) Even if the catalysts from different producers for a certain catalytic process have the similar compositions, the kinetic models describing their kinetic behaviour as a rule should be different. This means that the transition from one type of catalyst to another can not be made automatically without a lot of research efforts.

(ii) The commercial units always have a limited range for changes of operation parameters, like temperature, pressure, flow rate, concentrations at the reactor inlet and so on. They have limitations in production capacity, type of raw materials and energy use. This limitation can lead to rejection of the better catalyst for the existing process if its optimal regime needs parameters out of the range available in this particular unit.

(iii) Besides the technological and technical considerations economy should play decisive role in final selection.

The tests for selection of better catalyst for an existing process are performed in laboratory and pilot plant equipment.

3.3. DEVELOPMENT OF THE CATALYST FOR A NEW PROCESS

Testing a commercial catalyst for a new process is the most complicated case. Testing conditions are not as constrained as for testing of catalysts for the existing processes. However some limits should be imposed in order to meet some desired parameters like selectivity, safety limits, catalyst life resistance to deactivation and poisoning. Several steps should be passed until a new catalyst is selected.

(i) Screening. It is performed in order to select from all available samples the promising ones. Since the number of initial compositions is very big (usually not less than 500-1000 compositions) simple and fast testing procedure is needed. Of course if this case always is possible that some of the promising samples can be neglected. Therefore, a compromise between the comprehensive study and speed of testing is necessary.

(ii) Exploration. The samples selected during the screening are tested in big details by varying conditions in wide range of parameters. These tests should include also pilot plant experiments. Several best samples are selected at this stage of the catalyst development process.

The selected samples are further on objects of very detail examination, which include the following issues:

(i) Comprehensive kinetic model development uses the methods of experimental design and mathematical modelling.

(ii) Finding the best regimes of the catalyst pre-treatment in order to obtain catalyst with maximal activity and selectivity.

(iii) Design of catalyst grains (pellet, extrusions, and granules) and study the influence of heat and mass transfer processes on catalyst performance.

(iv) Kinetics of catalyst deactivation processes and estimation of the regimes for catalyst regeneration.

(v) Estimation of the life time of the catalyst due to pilot plant tests and proposing criteria for forecasting the catalyst life time

(vi) Safety transition regimes in cases of industrial accident

The best sample is finally tested in the industrial experimental unit. From this test data are collected which permit performing an optimal design of the industrial units.

3.4. NESSESARY INFORMATION ACOMPANING INDUSTRIAL CATALYSTS

Industrial catalysts should be offered on the market together with information about:
(i) reaction kinetics and kinetic model; (ii) catalytic activity and selectivity; (iii) catalyst pre-treatment regimes; (iv) catalyst deactivation kinetics with respect to different catalytic poisons; (v) catalyst regeneration regimes; (vi) catalyst lifetime: stability,

duration of operation, thermal stability; (vii) physicomechanical properties: impact strength, abrasion ability, hardness, surface area; (viii) hydrodynamic characteristics of the catalyst grain and of the catalyst bed in the reactor, determined by size, shape, density and porosity of the catalyst grains; (ix) safety transition regimes in cases of industrial accident; (x) economy of the process.

4. Catalytic Activity Tests

4.1. REQUIREMENTS FOR THE METHODS OF CATALYTIC ACTIVITY TESTS

In order to be able to obtain reliable and full information about tested catalysts the methods, which are used, have to conform to several criteria. In the same time the volume of obtained information should be sufficient to describe all characteristic features of the studied object.

Methods for the catalytic activity tests should be: (i) quantitative, (ii) precise, (iii) invariant regarding the apparatus used, (iv) standardised, (v) fast, and (vi) cheap.

4.2. THEORETICAL FUNDAMENTALS OF CATALYTIC ACTIVITY TESTS

The studies in the field of kinetics of heterogeneous catalytic reactions are an indispensable step of the theoretical and applied investigations on catalysis. They serve as fundamentals upon elucidation of the mechanism of the elementary act of a given heterogeneous reaction and contribute essentially to the elucidation of the catalyst behaviour in the course of its preparation, exploitation, and regeneration. The reaction kinetics serves as basis for development of methods for catalytic properties tests, during modelling and selection of optimal catalysts and optimisation of catalytic reactors. For these reasons the development of theory and practice in catalysis is inconceivable without unfolding extensive kinetic investigations.

4.3. ELEMENTS OF KINETICS OF COMPLEX CATALYTIC REACTIONS

From the point of view complexity of composition of reaction mixture and number of reactions taking place simultaneously, the catalytic processes under study can be divided on two groups: single route catalytic processes and multiroute catalytic processes.

(i) Single route catalytic processes. The stoichiometry of the single route catalytic processes is described by one stoichiometric equation. This group includes as most of petrochemical processes (hydrogenation processes). The aim of the catalytic tests are to measure the catalyst activity (the selectivity problem does not exist), as well as, to obtain all necessary information about catalyst behaviour, like catalyst deactivation, catalyst lifetime, etc. Analytical methods for concentration measurements and methods for treatment of the experimental data are relatively simple.

(ii) Multiroute catalytic processes. In order to have better understanding of the problems connected testing of catalysts for complex reaction systems we shall make introduction to the theory of kinetics of complex reactions. We shall call multiroute (complex) heterogeneous catalytic reaction a reaction system which consist of at least of two independent stoichiometric equations. Typical multiroute catalytic processes are all oil processing (cracking, reforming, hydrotreating and others), oxidation, dehydrogenation and isomerization processes. The aim of the tests is to measure the catalytic activity and selectivity on different reaction routes, as well as, to obtain all necessary information about catalyst behaviour, like catalyst deactivation, catalyst lifetime, etc. In many cases the selectivity is more important parameter than activity especially when environmental and economical consideration should be taken into account. Below the short information on equilibrium and kinetics in complex system is presented [14 - 18].

4.3.1. Equilibrium in complex chemical systems

If we have M reactions between N chemical species $A_{i,}$ we can write

$$\sum_{j}^{M} \sum_{i=1}^{N} \mu_{j,i} . A_i = 0 \qquad i = 1, 2, 3,....N \qquad j = 1, 2, 3,......., M \qquad (1)$$

where $\mu_{j,i}$ is stoichiometric coefficient of i^{th} specie in j^{th} reaction.

The maximum number of linearly independent chemical reactions, M_T, in a complex reaction system is given by:

$$M_T = N - q, \qquad (2)$$

where N is the total number of reagents in the system, q is the rank of the atomic matrix of the reagents.

The linearly independent chemical reactions create the so-called stoichiometric (thermodynamic) basis for the reaction system. All other chemical processes in the system can be expressed as a linear combination of these basic reactions and do not add any additional information about the reacting system. The stoichiometric basis is determined by the stoichiometry of the process, by the number and composition of the reagents, e.g. by quantities which can be directly determined experimentally.

4.3.2. Key reagents

For every independent reaction should exist a single reagent named key component. By measuring the concentrations of key reagents we are able to calculate the concentrations of the all reagents present in the reaction mixture. The selection of the key components usually is made by the convenience from the point of view of the experimental measurement.

4.3.3. Reacting species

The compounds participating in a heterogeneous catalytic reaction can be divided into two groups, viz. reagents and intermediate surface compounds (ISC). The reagents are the initial compounds and products of the reaction. Their concentrations or partial pressures can be determined at any moment of the reaction and at any point in the reaction space. The ISC are formed as a result of the chemisorption of reagents on the catalyst surface. Most of them have a very short lifetime. For each reagent at least one

ISC should be formed. The stoichiometry and structure of the ISC are not exactly known. In most of the cases, the concentrations of ISC can not be determined directly and they are expressed by concentrations or partial pressures of the reagents via adsorption isotherms.

4.3.4. Elementary steps

Every heterogeneous catalytic reaction proceeds via certain number of elementary reactions. Elementary reaction is the reaction in which, only one energy barrier is overcome. The stoichiometric coefficients of elementary reactions are integers. The rate of elementary reaction obeys the Law of Mass Action, or the Law of Surface Action, if the reactions take place at the surface of a catalyst. Arrhenius equation is strictly valid only for elementary reactions.

Two elementary reactions proceeding in forward and reverse directions form the elementary step. Three types of elementary steps are defined: mass-transfer steps, adsorption - desorption steps, and surface reaction steps. We shall deal with the latter two types of elementary steps. If the elementary reaction is irreversible, the elementary step consists of one elementary reaction. In elementary reactions participants are the ISC or the ISC together with reagents. Elementary reaction, whose rate depends linearly on the concentration of the ISC, will be called linear elementary reaction.

The rate of the s^th^ elementary reaction connecting the ISC α and ß

$$\sum_{j=1}^{m} \mu_{j,s} P_j + X_\alpha = \sum_{i=1}^{m'} \mu_{i,s} P_i + X_\beta \qquad (3)$$

may therefore be expressed as a difference between reaction rates of forward and reverse elementary steps

$$\mathrm{r}_s = r_s^+ - r_s^- = k_s^+ X_\alpha \prod_{j=1}^{m} P_j^{\mu_{js}} - k_s^- X_\beta \prod_{i=1}^{m'} P_i^{\mu_{is}} \qquad (4)$$

where r_s is the rate of the s^{th} elementary reaction, X_α and X_β are the concentrations of ISC α and β involved in the s^{th} step, P_j and P_i are the concentrations of the j^{th} and i^{th} reagents participating in the s^{th} elementary step, $\mu_{j,s}$ and $\mu_{i,s}$ are the stoichiometric coefficients of the j^{th} and i^{th} reagents participating in the s^{th} elementary step, m and m' are the number of reagents taking part in the forward and reverse elementary reactions of the s^{th} step.

Existing experimental data show, that in most of the cases in elementary reactions μ_{js} and μ_{is} = 0 or 1, and m and m' = 0 or 1. In this case equation (3) can be expressed as:

$$P_j + X_\alpha = P_i + X_\beta \qquad \text{or} \qquad X_\alpha = X_\beta \qquad (5)$$

and eq. (4) will take the form:

$$r_s = k_s^+ X_\alpha P_j - k_s^- X_\beta P_i \quad \text{or} \quad r = k_s^+ X_\alpha - k_s^- X_\beta \tag{6}$$

depending on whether the reagents participates in the sth elementary reaction or not.

If sth elementary step is irreversible then eq. (4) become

$$r_s = k_s X_\alpha \prod_{j=1}^{m} P_j^{\mu_{j,s}} \tag{7}$$

and eq. (6) has the forms

$$r_s = k_s X_\alpha P_j \qquad \text{or} \qquad r_s = k_s X_\alpha, \tag{8}$$

4.3.5. Reaction mechanism

The set of elementary reactions that allows a qualitative and quantitative description of major characteristics of the process studied to be made, will be named the mechanism of chemical reaction. A mechanism consisting only of linear steps will be described as a linear mechanism. A large number of reactions proceed via non-linear mechanism, e.g. they include elementary reactions, having rates that depend non-linear on the concentration of the ISC. The mechanism of process of selective I) and total II) oxidation of ethylene on a silver catalyst given below is an examples of mechanism containing linear [1) and 2)] and non-linear [3) and 4)] steps [19].

$$\begin{array}{lcc}
 & \underline{\text{I}} & \underline{\text{II}} \\
1)\ Z + O_2 = ZO_2 & 2 & 0 \\
2)\ ZO_2 + C_2H_4 \rightarrow ZO + C_2H_4O & 2 & 0 \\
3)\ 2ZO = 2Z + O_2 & 1 & -3 \\
\underline{4)\ C_2H_4 + 6ZO \rightarrow 2CO_2 + H_2O + 6Z} & \underline{0} & \underline{1} \\
\text{I)}\ 2C_2H_4 + O_2 = 2C_2H_4O & & \\
\text{II)}\ C_2H_4 + 3O_2 = 2CO_2 + 2H_2O & &
\end{array} \tag{9}$$

4.3.6. Reaction routes

Complex reactions can be expressed as a manifold of elementary steps and ISC combination, which in certain conditions give different reaction pathways with producing the same or different products. Such pathways are named reaction routes. For one proceeding of certain reaction route every step must participate, as many time as, is its stoichiometric number. Summing stoichiometric equations of elementary steps in given route multiplied by their stoichiometric numbers one should obtained stoichiometric equation of the route. Reaction rate on the reaction route is equal to the number of realisation of reaction route in unit of time.

The reaction scheme or reaction mechanism for a single reaction can be presented by:

$$\sum_{s=1}^{S}\sum_{j=1}^{N}\left(\nu_{s,j}.A_j+\xi_{s,j}.Z_j\right)=0 \tag{10}$$

where $\nu_{s,j}$ is the stoichiometric coefficient of the jth reagent A_j in the sth elementary step. $\nu_{s,j}$ is related to the stoichiometric coefficient of jth reagent in the stoichiometric equation of the reaction by the equation

$$\sum_{s=1}^{S}\nu_{s,j}.\sigma_s=\mu_j \tag{11}$$

where $\xi_{s,j}$ is the stoichiometric coefficient of the jth ISC Z_j in the sth elementary step. For $\xi_{s,j}$ is valid the equation

$$\sum_{s=1}^{S}\xi_{s,j}.\sigma_s=0 \tag{12}$$

where σ_s is the stoichiometric number of the step s from the reaction mechanism.

The stoichiometric number shows how many times a given elementary reaction should be repeated in order to have one turnover of the main reaction. For the mechanism (9) stoichiometric numbers are given at the right side of every elementary step. Stoichiometric number equal to zero means that this particular elementary step do not take part in the reaction route. Negative sign of the stoichiometric number means that this elementary step should be read from right to the left. Mechanism (9) is an example for two route mechanisms. Every route has its own set of stoichiometric numbers. The first route consist of steps 1), 2), and 3) with stoichiometric numbers $\sigma_1^{(1)}$ = 2, $\sigma_2^{(1)}$ = 2, and $\sigma_3^{(1)}$ = 1. The second route consist of steps 3) and 4) with stoichiometric numbers $\sigma_3^{(2)}$ = -3 and $\sigma_4^{(2)}$ = 1. The third elementary step participates in both routes with different stoichiometric numbers. The sign minus of $\sigma_3^{(2)}$ mean that elementary step 3) in the second route is proceeding in the reverse direction.

If an elementary step s is part of one route mechanism, its rate r_s will be given by the difference in the rates of elementary reactions in the forward r_s^+ and reverse r_s^- directions:

$$r_s = r_s^+ - r_s^- = \sigma_s R, \tag{13}$$

where σ_s is the stoichiometric number of the elementary step s in the reaction mechanism, and R is the reaction rate along the route.

If the elementary step forms part of P routes mechanism, the rate of the elementary step r_s will equal the sum of the rates along the different routes in which the elementary step participate, multiplied by the stoichiometric number $\sigma_s^{(P)}$ of the elementary step for the given route:

$$r_s = r_s^+ - r_s^- = \sum_{p=1}^{P} \sigma_s^{(P)} R^{(P)} \tag{14}$$

where $\sigma_s^{(P)}$ is the stoichiometric number of the elementary step s for the P^th^ route, $R^{(P)}$ is the reaction rate along the P^th^ route, and P is the number of routes, in which participate the elementary step s.

4.3.7. Horiuti's rule

The number of independent routes in a given system depends upon our knowledge about the studied process, complexity and structure of the proposed reaction mechanism. According to Horiuti's rule, which is valid, both for linear and non-linear mechanisms, the number of independent routes M_K in a complex reaction system is given by the expression:

$$M_K = S - L, \tag{15}$$

where S is the number of elementary steps in the reaction mechanism, and L is the number of independent ISC taking part in the reaction mechanism.

The surface concentrations of the ISC are interconnected by the balance equation: and for L we have:

$$L = L_{tot} - 1, \tag{16}$$

and finally we obtain:

$$M_K = S - L_{tot} + 1. \tag{17}$$

The reaction basis given by equation (26) is named kinetic basis. It consists of the routes obtained from proposed reaction mechanism. Their number is different for different mechanisms and depends on the details of the mechanism. It is obvious that

$$M_K \geq M_T , \tag{18}$$

which means that some of the routes of the kinetic basis are dependent from thermodynamic point of view. In this case reaction mechanism should be changed in such a way that thermodynamic and kinetic basis become equal. If the reaction mechanism preserve the number of elementary steps and ISC, the difference M_K - M_T gives the number of so called nullroutes. Such a route has stoichiometric equation 0=0 but its rate is different from zero.

The rate of the reaction on stoichiometric independent routes (which we can not measure experimentally) is calculated from the reaction rates for the individual reagents in the system (which can be measured directly during the experiment) using the equation:

$$r_i = \sum_{j=1}^{M_T} \left\| \mu_{i,j} \right\|^T R_j \tag{19}$$

where r_i is the reaction rate for ith reagent, i = 1,2,....,n is the number of the reagents in the system, Rj is the reaction rate along the stoichiometric linearly independent route j, j = 1,2,.....,M_T, $\left\| \mu_{i,j} \right\|^T$ is an element of transposed stoichiometric matrix. Each element $\left\| \mu_{i,j} \right\|^T$ of the stoichiometric matrix gives the stoichiometric coefficient of i^{th} reagent in j^{th} reaction independent route.

We now illustrate what has been said so far by an example:

	I	II	III	IV
1). 1-C_4H_8 + Z = 1-C_4H_8Z	1	1	0	0
2). cis-2-C_4H_8 + Z = cis-2-C_4H_8Z	-1	0	1	0
3). trans-2-C_4H_8 + Z = trans-2-C_4H_8Z	0	-1	-1	0
4). 1-C_4H_8Z = cis-2-C_4H_8Z	1	0	0	1
5). 1-C_4H_8Z = trans-2-C_4H_8Z	0	1	0	-1
6). cis-2-C_4H_8Z = trans-2-C_4H_8Z	0	0	1	1

I). 1-C_4H_8 = cis-2-C_4H_8
II). 1-C_4H_8 = trans-2-C_4H_8
III). cis-2-C_4H_8 = trans-2-C_4H_8
IV). 0 = 0

(20)

Here Z is a free site on the catalyst surface, and 1-C_4H_8Z, cis-C_4H_8Z, and trans-C_4H_8Z are ISC for three butenes.

For this particular mechanism the stoichiometric basis and the route basis are given by following equation:

$$M_T = 3 - 1 = 2 \quad \text{and} \quad M_K = 6 - 4 + 1 = 3 \tag{21}$$

We have two stoichiometric independent routes in the thermodynamic basis and three independent routes in the kinetic basis of this mechanism. It follows that one route of kinetic basis is stoichiometric dependent. If we accept that the third route is stoichiometric dependent two opportunities exist for making M_T equal to M_K:

i) To remove from the mechanism one elementary step so M_K= 5 - 4 + 1 = 2

ii) To change the stoichiometric numbers of the elementary steps participating in the third route that it will turn to null route. Such opportunity is presented as route IV). The reaction along this route proceeds at a finite rate without influencing the stoichiometry of the process.

The relationship between the reaction rates for the reagents and the rates along the linearly independent stoichiometric routes may be expressed by the following system:

$$\begin{aligned} r_1 &= - R_1 - R_2 \\ r_2 &= R_1 \\ r_3 &= R_2 \end{aligned} \qquad (22)$$

If we take into account the third stoichiometric dependent route the system (22) becomes

$$\begin{aligned} r_1 &= - R_1 - R_2 \\ r_2 &= R_1 - R_3 \\ r_3 &= R_2 + R_3 \end{aligned}$$

where the reagents labelled 1 to 3 is, respectively, 1-butene, cis-2-butene, and trans-2-butene.

4.3.8. Steady state approximation

The steady state regime of the proceeding of given chemical process can be realised only in open systems. The steady state regime means that all reaction parameters (concentrations of reagents and ISC, temperatures, partial and total pressure, reagents flow rate) should have constant values which do not change with time. This however does not mean that the parameters should have the same value at different points of the reaction space.

For every ISC we can write

$$\frac{dX_i}{dt} = F\left(c_j, X_K\right) \qquad (23)$$

where $F(c_j, x_k)$ is the function which allow us to express the concentrations of ISC via the concentrations of the reagents, j = 1, 2, ...,N is the number of reagents in the system, i = 1, 2, ..., K is the number of ISC formed on the catalyst surface and included in the reaction mechanism, $K \geq N+1$ because free catalyst surface should be taken into account.

At steady state regime $dX/dt = 0$ which means that the realisation of the steady state regime leads to very important simplification in the treatment of kinetic problems. In order to find all concentrations of ISC instead of solving the system (one equation for every ISC) of differential equations (24), we have to solve the system containing the same number of algebraic equations.

$$\sum F.(c_j, X_K) = 0 \qquad (24)$$

and substantially to simplify the problem.

At steady state the reaction rates of all consecutive elementary steps should be approximately equal to each other and equal to the slowest one called limiting reaction step. For the each step we can write

$$r_1^+ - r_1^- = \sigma_1 r,\; r_2^+ - r_2^- = \sigma_2 r ,...,\; r_s^+ - r_s^- = \sigma_s r \,,\; r_L^+ - r_L^- = \sigma_L r \; (25)$$

$$\mathrm{r} = \frac{r_1^+ - r_1^-}{\sigma_1} = \frac{r_2^+ - r_2^-}{\sigma_2} = ...= \frac{r_s^+ - r_s^-}{\sigma_s} = \frac{r_L^+ - r_L^-}{\sigma_L} \qquad (26)$$

where r_s^+, r_s^- are the reaction rates in the forward and reverse directions of the s$^{\mathrm{th}}$ elementary step, σ_s is the stoichiometric number of the s$^{\mathrm{th}}$ elementary steps. The stoichiometric numbers vary usually between 1 and 3.

From eq. (14) follows that any elementary step can take part in different reaction routes of the reaction mechanism

$$\mathrm{r_s} = r_s^+ - r_s^- = \sum_{p=1}^{P} \sigma_s^{(P)} R^{(P)} \qquad (14)$$

Therefore the difference between the rates of the elementary steps can reach one order of magnitude. This difference depends upon the numbers of reaction routes and values of the stoichiometric numbers in every one of them.

4.3.9. Application of the conditions for steady state for deriving the reaction rate equations.

Applying eq. (26) for the reaction mechanism which consist of s elementary steps we can write equation

$$r = \frac{r_1^+ r_2^+ \ldots r_s^+ - r_1^- r_2^- \ldots r_s^-}{\sigma_1 r_2^+ \ldots r_s^+ + r_1^- \sigma_2 r_3^+ \ldots r_s^+ + \ldots + r_1^- r_2^- \ldots r_{s-1}^- \sigma_s} \qquad (27)$$

in which the overall rate is expressed by the rates of the elementary reactions participating in the reaction mechanism. In traditional the form reaction rate equation is expresses by the equation:

$$\mathbf{r} = \mathbf{F}(\mathbf{c}, \mathrm{T}) \qquad (28)$$

where **r** is a vector of the reaction rates on the independent reaction routes, **c** is a vector of reagents' concentrations. The reaction rate (or rates on independent stoichiometric routes) at constant temperature and catalyst activity depends only on the changes of reagents' concentrations. From point of view of the reaction mechanism the measured reaction rate is equal to the rate of slowest step in the reaction mechanism so-called rate limiting step (rate limiting steps, in case of complex reaction system, the number of which is equal to the number of independent routes).

Equation (27) can be rearranged in form, which is very convenient for practical applications.

$$r\left(\frac{\sigma_1}{r_1^+}+\frac{r_1^-\sigma_2}{r_1^+r_2^+}+\dots\dots\frac{r_1^-r_2^-\dots\dots r_{s-1}^-\sigma_s}{r_1^+r_2^+\dots\dots r_s^+}\right)=1-\frac{r_1^-r_2^-\dots\dots r_s^-}{r_1^+r_2^+\dots\dots r_s^+} \qquad (29)$$

If in the system we have P reaction routes the equation (29) have the following form

$$\sum_{p=1}^{P} r^{(P)}\left(\frac{\sigma_1^{(P)}}{r_1^+}+\frac{r_1^-\sigma_2^{(P)}}{r_1^+r_2^+}+\dots\dots\frac{r_1^-r_2^-\dots\dots r_{s-1}^-\sigma_s^{(P)}}{r_1^+r_2^+\dots\dots r_s^+}\right)=1-\frac{r_1^-r_2^-\dots\dots r_s^-}{r_1^+r_2^+\dots\dots r_s^+} \qquad (30)$$

In every term of the left side of the eq. (29) and (30) correspond to a given ISC. Except for the first term, in the other terms the nominator contains the rates for the reversed direction for the previous steps and denominator contains all the rates for the following steps for forward directions. It means that the ISC produced in the steps in the nominator are consumed by the steps in the denominator and these concentrations disappear from the equation except the ISC produced in the first step. In order to obtain equations for all ISC in the system we have to change consecutively the number of the steps in such way that every step should appear once as a number one.

Let have a reaction with one route mechanism.

$$\begin{array}{ll} \text{1). } A + Z = Z_1 & \sigma_1 = 1 \\ \text{2). } Z_1 + B = Z_2 & \sigma_2 = 1 \\ \underline{\text{3). } Z_2 = C + Z} & \underline{\sigma_3 = 1} \\ \quad A + B = C & \end{array} \qquad (31)$$

According to the Mass Action Law the reaction rates of elementary reactions in the mechanism (31) are:

$$\begin{array}{ll} r_1^+ = k_1^+ P_A Z & r_1^- = k_1^- Z_1 \\ r_2^+ = k_2^+ P_B Z_1 & r_2^- = k_2^- Z_2 \\ r_3^+ = k_3^+ Z_2 & r_3^- = k_3^- P_C Z \end{array} \qquad (32)$$

where Z, is the empty part of the catalyst surface, Z_1, and Z_2 are the surface concentrations of the ISC participating in the reaction mechanism. The ISC are connected by a balance equation $Z + Z_1 + Z_2 = 1$

Inserting these expressions into the balance equation and accepting for simplicity that the second step of the reaction mechanism is irreversible i.e. $r_2^- = 0$, we find the expression for the reaction rate equation.

$$r = \frac{k_1^+k_2^+k_3^+P_AP_B}{k_1^+k_3^+P_A + k_2^+k_3^+P_B + k_1^+k_2^+P_AP_B} \qquad (33)$$

For written in traditional form

$$r = \frac{k_1 P_A P_B}{k_2 P_A + k_3 P_B + k_4 P_A P_B} \qquad (34)$$

All constants in the equation (34) have a complex character and are expressed by the different functions of the constants of the elementary reactions. For this reason the Arrhenius equation can be used for description of the dependence of the overall reaction rate from the temperature only as a approximation but not as a exact law.

In order to find the values of the reaction rate constants of the elementary steps we need an additional information which can be obtained from non steady state kinetic measurements and from other experimental and theoretical methods like chemisorption, quantum chemistry and surface science methods. Parameter estimation needs application of statistical and non-linear programming methods.

4.4. PROBLEMS IN KINETICS OF CATALYTIC REACTIONS

The tasks that face now the researchers in the field of catalytic reaction kinetics could be formulated in general as follows:

(i) Development of the theory of kinetics. The investigations in this direction give impetus to theoretical aspects of the kinetics, the methods of constructing kinetic models, the methods of evaluation of kinetic parameters and the mathematical problems, connected with it.

(ii) Kinetics and mechanism of important in theoretical aspect catalytic processes. These studies aim at assisting the development of theory in catalysis, the selection of new catalytic systems and catalysts, elucidation of the intimate mechanism of the catalytic act, the nature of the active site, the behaviour of the catalyst - reagent system as a whole etc.

(iii) Creation of kinetic models of industrially important reactions. The kinetic models of catalytic processes are the basis, on which the modelling and the design of catalytic reactors are carried out. The transition from molecular scale to macro - scale during the practical realisation of a given catalytic process is accomplished on this basis. That is why it is necessary that the mathematical model be able to reflect all essential aspects of the mechanism of the studies process.

(iv) Development of kinetic models of nonstationary catalytic processes. These models account for the following factors; the rates of the elementary chemical transformations, the rate of changing the composition and the activity of the catalyst, diffusion of the surface species, transfer of reactants from one type of active sites to others, the interconnection between the catalytic properties and the catalytic parameters etc. The investigation of the dynamics of the catalytic process i.e. the evolution of the heterogeneous catalytic reactions is included in this set of tasks. It is on these results that the development of the studies on the dynamics and stability of the catalytic reactors is depending, which in their turn determine the optimal starting and operation conditions.

(v) The elaboration of theoretically grounded methods for testing and controlling the catalytic activity and selectivity of the industrial catalysts. Due to the strongly specific effect of the catalysts it is not possible to propose universal methods for testing and controlling their catalytic activity and selectivity. These methods are individual for each catalytic system. For this reason the elaboration, unification and standardisation of these methods has great importance for the correct selection and evaluation of the studied catalysts.

(vi) The kinetics of topochemical processes, occurring during the preparation, exploitation and regeneration of the industrial catalysts. In the course of preparation, operation and regeneration of the catalysts a series of processes are proceeding in them, which lead to alteration of their properties. The good knowledge and control of this type of alteration may bring considerable improvement of the quality of the catalysts and optimisation of the regime of their exploitation.

(vii) Theory and automation of the experiment. Computer application. The experimental studies in the field of chemical kinetics consume a large volume of research work and they are expensive. They require especially high degree of experience in order to set the task correctly and to select the experimental design. The dynamic development of the industrial catalysis puts on the agenda the problem to increase essentially the rate of kinetic model construction. The solving of this problem is unthinkable without applying the achievements of the optimal experiment theory, the use of automated systems for carrying out the kinetic experiments and data acquisition on the basis of modern computers during all stages of obtaining and processing the experimental data.

4.5. SOURCES OF EXPERIMENTAL ERRORS IN CATALYTIC ACTIVITY TESTS

The sources of experimental errors during the catalytic activity measurements are result of influence of many factors:

(i) Quality of raw materials for the catalyst preparation.

(ii) Technology of the catalyst production

(iii) Inhomogenity of catalyst samples due to the process of the catalyst preparation.

(iv) Quality of the reactants.

(v) Inhomogenity of catalyst samples due to the processes of the catalyst pretreatments and regeneration.

(vi) Changes in the reaction parameters during the catalytic tests.

(vii) Quality and preciseness of the analytical methods and other equipment.

(viii) Type and quality of the selected of reactors

(ix) Heat and mass transfer influence.

4.5.1. Raw materials for catalyst production

Raw materials selected for catalyst production should satisfy certain criteria: (i) constant chemical and phase composition; (ii) absence of undesired components; (iii) specific particle size; (iv) available technological equipment; (v) low price.

Reproducibility of the catalyst quality and homogeneity depend on these criteria and on the technological regimes used. To keep catalyst prices as low as possible, it is very important to establish the utmost amount of undesired components present in the raw materials, which does not have any harmful effect on catalyst quality. This amount is dependent on the specific sensitivity of every catalyst toward catalytic poisons.

Usually salts, like sulphates, chlorides, nitrates, carbonates and hydroxides are used for catalyst preparation. The selection of suitable raw materials should be made on the basis of solubility, decomposition temperature and environmental protection considerations.

4.5.2. Technology and unit operations in catalyst production

The selection of best technology for a certain catalyst production should be made bearing in mind the parameters of different steps of the technology to be achieved, chemicals properties, necessary equipment and economy of the production. The unit for catalyst production has to be flexible; this means that several catalysts should be produced on one industrial unit.

The unit operations used in catalyst preparation can be classified in several groups: (i) hydrodynamic processes: liquid and suspension transportation, separation of suspension, mixing of liquids and suspensions; (ii) heat processes: heating, cooling, and evaporation of liquids, calcination, and steam condensation; (iii) mass transfer processes: extraction, adsorption, drying, crystallisation, and dissolution of solid chemicals; (iv) mechanical processes: formation of catalyst grains, granulation, solid particles transportation, crushing, grinding, and sieving; (v) chemical processes are diverse and depend on the nature of the chemical compounds in the system. The chemical processes generally can proceed in a homogeneous phase (gas, liquid) or in the heterogeneous systems: gas-liquid, gas-solid, liquid-solid. During calcination procedure topochemical processes take place.

4.5.3. Inhomogenity of catalyst samples due to the process of the catalyst preparation

In order to obtain reliable and reproducible results from the measurements of the catalytic properties of industrial catalysts it is very important to use a large catalyst probe (taken as mean probe according to the standardised sampling procedure) as a source of catalyst charges for laboratory reactors. Industrial catalysts grain - pellets, extrusions, granules, and microspheres for fluidised bed reactors are not ideally homogeneous. For example, samples taken from the top and the bottom of the tank in which they are transported and stored are usually not identical. The same is valid for samples taken from different tanks or different charges.

4.5.4. Quality of the reactants

When a screening analysis is performed usually pure gas mixtures are used. For pilot plant tests reaction mixtures coming from industrial unit are preferable, because the every industrial reaction mixture contains specific microimpurities, which some times can play an important influence on catalyst performance.

4.5.5. Inhomogenity of catalyst samples due to the processes of the catalyst pretreatments and regeneration

In order to assure reproducibility of the experimental results it is very important to accept a standard optimal procedure for catalyst pre-treatment and regeneration. This problem is of vital importance in the case of testing catalysts with different chemical composition. It is not possible to use the same approach for different catalysts.

4.5.6. Changes in the reaction parameters during the catalytic tests

Nowadays catalytic activity is determined with an average experimental error about 10-15% and selectivity - 1-2%. It is necessary to increase the precision of the determination the reaction rate to ± 1 - 5%. We shall shortly discuss the major sources of experimental errors obtained due to changes of the reaction parameters [4].

At steady state regime in flow reactor the reaction rate is estimated from the equation:

$$r = \frac{1}{W}(F.C - F_o.C_o) \tag{35}$$

where r is the reaction rate, W is the catalyst weight, F_o and F are the flow rates at the reactor inlet and outlet, C and C_o are the concentrations at the reactor inlet and outlet. From this equation we can write the equation for error calculation of the catalytic activity measurement. For the products of reaction not present in the reaction mixture at the inlet of the reactor we have

$$\Delta_r^2 = \Delta_g^2 + \Delta_F^2 + \Delta_C^2 \tag{36}$$

where Δ^2 is the mean square relative error, indices r, g, F, C correspond to the reaction rate, catalyst weight, flow rate and concentration. Error for catalyst weight measurement is negligible and therefore main sources of errors are regulation and measurement of flow rates and estimation of reagent concentration.

For the reactants at the reactor exit the error depends also on the degree of conversion:

$$\Delta_r^2 = \Delta_g^2 + \frac{1}{x^2}(\Delta_{Fo}^2 + \Delta_{Co}^2) + (\frac{1-x}{x})^2(\Delta_F^2 + \Delta_C^2) \tag{37}$$

At high degree of conversion the experimental error for reaction rate measurement depends mainly on the errors in regulation and measurement of the flow rates and on the estimation of concentrations at the inlet and outlet of the reactor.

For selectivity defined as

$$S = \frac{F.C}{F_o.C_o - F.C} \tag{38}$$

we have

$$\Delta_S^2 = \Delta_C^2 + \left(\frac{2x-1}{x}\right)^2 . \Delta_F^2 + \frac{1}{x^2}(\Delta_{Fo}^2 + \Delta_{Co}^2) + \left(\frac{1-x}{x}\right)^2 \Delta_C^2 \qquad (39)$$

At high degree of conversion we have:

$$\Delta_S^2 = \Delta_{Co}^2 + \Delta_F^3 + \Delta_{Fo}^2 + \Delta_C^2 \qquad (40)$$

At high degree of conversion the experimental error for selectivity measurement depends mainly on the errors in regulation and measurement of the flow rates and on the estimation of concentrations at the inlet and outlet of the reactor.

The error in temperature regulation is given by:

$$\Delta_r^2 = \left(\frac{E}{RT}\right)^2 . \Delta_T^2 \qquad (41)$$

4.5.7. Quality and preciseness of the analytical methods and other equipment.

From the above discussion it follows that sources of experimental errors in catalysts activity measurements are the flow rate regulation and measurements, regulation of the temperature regime, analytical control.

The most common analytical methods used to determine reaction mixture composition is gas chromatography. The precision of modern gas chromatographs is in the range of 0.05 to 0.1 %. The reactor temperature can be easily kept constant within limits ± 0.1-0.5 ^{o}C. It follows that the main source of experimental errors, are the flow rate regulation and measurements. Therefore it is of vital importance to have very precise devices for flow control and measurement. If the catalytic tests are performed at high pressure we have to take into account that the stable regulation and measurement of the pressure is also serious source of experimental errors.

4.6. DEVELOPMENT AND STANDARDIZATION OF METHODS FOR CATALYSTS CHARACTERIZATION

This is very important and very difficult for solving problem. Due to the strongly specific action of the catalysts it is not possible to propose universal methods for testing and controlling their catalytic activity and selectivity. These methods are individual for each catalytic system. For this reason the elaboration, unification and standardisation of these methods has great importance for the correct selection and evaluation of the studied catalysts. The following tasks are included:

(i) Development of the standard methods for controlling the physicochemical and physico-mechanical properties - surface area, porosity and dispersion structure, strength to pressure, abrasion ability, stability to thermal, mechanical and chemical erosion, strength to strikes, thermal conductivity and others.

(ii) Development of the standard laboratory methods for controlling the catalytic properties - activity, selectivity, stability to catalytic poisons, duration of operation, cooking and regeneration. These methods should be selected in such a way that based on them we should be able to make a realistic evaluation of the catalyst quality and its behaviour under industrial conditions.

(iii) the testing of the physicochemical, physico-mechanical and catalytic properties of the catalysts required the elaboration, construction and standardisation of the respective appliances and devices for automation. The development of this equipment should be the task both of catalysis research workers and of engineers, working on the problems of apparatus construction.

5. Laboratory reactors

Due to the limited space of this paper we can not enter into details in this area, but shall discuss in general terms some advantages and disadvantages of different types of laboratory reactors [3 - 7, 16].

5.1. CLOSED (BATCH) REACTOR

Basic principle - integral reactor
Main requirement - ideal mixing
Basic condition - quasi steady state
Typical gradients - concentration with time
Advantages - small amount of reactant, precision of measurements, obtaining full kinetic curve in one experiment
Disadvantages - difficulties in achieving quasi steady state, no direct measurement of the reaction rate.

Reaction rate can be estimated from the equation

$$t = N_o \int_0^x \frac{dx}{r.W} \tag{42}$$

5.2. FLOW REACTOR

Basic principle - integral reactor
Main requirement - ideal plug flow
Basic condition - steady state
Typical gradients - radial and longitudinal gradients of concentration and temperature, the catalyst bypassing, channelling near the reactor wall.
Advantages - similarity to industrial units, simple equipment
Disadvantages - difficulties in achieving quasi steady state, no direct measurement of the reaction rate, many gradients
Reaction rate can be estimated from the equation

$$\frac{W}{F} = \int_0^x \frac{dx}{r} \tag{43}$$

5.3. DIFFERENTIAL REACTOR

Basic principle - differential reactor
Main requirement - ideal plug flow
Basic condition - steady state, low degree of conversion up to 10 %, high space velocity
Typical gradients - radial and longitudinal gradients of concentration and temperature
Advantages - opportunity to measure directly the reaction rate, similarity to industrial units, simple equipment.
Disadvantages - difficulties in achieving quasi steady state, existence of some gradients, difficult to apply for multiroute catalytic processes.
Reaction rate is estimated from the equation:

$$r = \frac{F.\Delta x}{W} \tag{44}$$

5.4. GRADIENTLESS REACTOR

Basic principle - differential reactor
Main requirement - ideal mixing
Basic condition - rate of mixing >> flow rate
Typical gradients - in some cases gradients due to internal diffusion limitations
Advantages - direct measurement of reaction rate at any degree of conversion, absence of gradients. By increasing the circulation rate mass velocity can be increased without changing the flow rate F and, consequently the contact time W/F and the overall space velocity remain unchanged. The opposite is also possible, keeping the circulation rate, mass velocity remain unchanged even if flow rate F, and with it the overall space velocity and constant time, is changed. Gradientless reactor permits with small fresh feed and small quantity of catalyst to achieve mass velocities of commercial reactors. It is possible to separate the concentration and temperature terms and to measure the apparent energy of activation even when the concentration dependency is not known. If two experiments are made at two temperatures and the same discharge concentration is the same (at different feed rates) than the effect is attributed to temperature.
Disadvantages - complicated equipment, not suitable for reaction with fast deactivating catalyst. The greatest difficulty with gradientless reactors is that discharge concentrations should be the independent variables along with temperature, while feed rate and even feed compositions will be dependent variables. In practical terms, this means that feed rate and feed composition have to be changed until the desired exit values are reached. In this sense contact time, or space velocities, becomes a dependent variable.
Reaction rate in gradientless reactor is estimated from the equation:

$$r = \frac{F.\Delta x}{W} \tag{44}$$

6. Influence of heat and mass transfer on the proceeding of the heterogeneous catalytic reactions

Heterogeneous catalytic reactions are always connected with processes of mass and heat transfer. If these processes are fast enough they do not have any substantial influence on the proceeding of the catalytic processes. When, however, these processes are slow enough the situation becomes different. Under steady state conditions the rates of all consecutive steps should be equal to one another and equal to the slowest one. Since the diffusion steps are the slowest one, the overall reaction rate will be equal to the rate of the diffusion. In this case, the overall reaction rate will not be connected with the reaction mechanism but will be determined by the rate of physical processes. It is clear that the processes of mass transfer can have a substantial effect on the proceeding of heterogeneous catalytic reactions. Therefore, it is obvious, that the study of the influence of the processes of mass and heat transfer on the proceeding of heterogeneous catalytic reactions has a great theoretical and practical importance [20-24].

6.1. TYPES OF KINETIC REGIMES

The following different regimes for proceeding of heterogeneous catalytic reaction may be observed:

- Kinetic regime in which the intrinsic surface reactions are the slowest and determine the overall reaction rate;
- External diffusion regime in which the processes of mass transfer of the reagents and product of the reaction to and from the external catalyst surface are the slowest and determine the overall reaction rate;
- Internal diffusion regime in which the processes of mass transfer of the reagents and product of the reaction within the pores of catalyst particles are the slowest and determine the overall reaction rate;
- Transition regime in which both the chemical and mass transfer processes have approximately equal rates and the overall reaction rate is determined by the proceeding of the intrinsic surface reactions and diffusion.

6.2. FUNDAMENTAL LAWS OF TRANSPORT PHENOMENA.

In a stagnant binary gas mixture, according to the Fick's first law, the molar flux J [mol/cm^2.sec] is proportional to the concentration gradient in the direction x of the diffusion

$$J_1 = -D_{12}\frac{dc_1}{dx} = -D_{12}.c_{tot}\frac{dY_1}{dx} \tag{45}$$

c_1 is the molar concentration of the component 1, c_{tot} is the total molar concentration of the mixture, Y_1 is the mole part of the component 1, D_{12} (cm^2/sec) is the diffusion coefficient for 1 diffusing in gas 2, x is the direction of the mass flow due to diffusion. Diffusion coefficient is a function of the molecular properties of the two gases and increases with increase in temperature or decrease in pressure. It varies little with the mole fractions of the two gases but it varies more with the changes in the total molar concentration of the gas mixture c_t.

The heat flow q [cal.cm^{-2}.sec^{-1}] from high to low temperature regions according to the Fourier's law is determined by the following equation:

$$q = -k_t \frac{dT}{dx} \tag{46}$$

where k_t is the thermal conductivity of the fluid, T is the absolute temperature, x is the direction of the heat flow.

The kinetic molecular theory gives the following expressions for D_{12} [cm^2.sec^{-1}] and k_t

$$D_{12} = \frac{1.858x10^{-3}\sqrt{\frac{T^3.(M_1 + M_2)}{M_1.M_2}}}{P\sigma_{12}^2\Omega_D} \tag{47}$$

$$k_t = 1.989x10^{-4}\frac{\sqrt{T/M}}{\sigma^2.\Omega_\mu} \tag{48}$$

where M_1 and M_2 is molecular weight, σ is the kinetic diameter of the molecules, Ω_μ and Ω_D are corresponding collision integrals, T is the absolute temperature.

A fluid passing over the surface of a pellet forms a boundary layer in which the velocity parallel to the surface varies rapidly over a very short distance normal to the flow. At the solid surface the fluid velocity is zero, but approaches the bulk-stream velocity in the distance less than millimetre away from the surface. In this thin layer the mass and heat transfer are proceeding via molecular diffusion, while in the main fluid stream mass transfer is essentially independent of the molecular diffusion coefficient D_{1m}. The overall mass transport is proportional to D_{1m}, where 0<n<1. The molal flow rate N [mol.cm^{-2}.sec^{-1}] is given by

$$N = k_c.(C_o - C_s) \tag{49}$$

where N is the diffusion flux fluid to solid, k_c is the coefficient of mass transfer, C_s is the concentration at the surface, C_o is the concentration in the ambient bulk fluid. In gas system instead of concentrations partial pressures should be used

$$N = k_G.(p_o - p_s) \tag{50}$$

where $k_G = k_c/RT$. k_G and k_c are related to the molecular diffusion coefficient D_{12} and the thickness of the boundary layer δ by the following relation:

$$k_c = D_{12}/\delta.k_G = D_{12}/\delta.RT \tag{51}$$

The heat flow through the boundary layer can be expressed as:

$$q = h.(T_b - T_s) \tag{52}$$

where h is the heat transfer coefficient related to the thermal conductivity of the fluid and to the size of the boundary layer.

The data on mass and heat transfer between the bulk stream and particle surface can be presented by the use of dimensionless groups. For mass transfer phenomena three dimensionless criteria can be defined:

(i) Reynolds number

$$Re = G.d_p/\mu, \tag{53}$$

(ii) Schmidt number

$$Sc = \mu/D.\rho, \tag{54}$$

(iii) Sherwood number

$$Sh = k_c.\rho/G \tag{55}$$

The coefficient of mass transfer k_c can be estimated by using the so-called j-factor defined by the following expression:

$$j_D = Sh.Sc^{3/2} = (\alpha/\varepsilon)Re^{-\beta} \tag{56}$$

$$k_c = \frac{\alpha.\mathrm{Re}^{-\beta}.G.D^{3/2}.\rho^{1/2}}{\varepsilon.M^{3/2}} = j_D.G.D^{3/2}.\rho^{1/2} \tag{57}$$

where G is the mass velocity based upon cross-sectional area of empty reactor, μ is the viscosity of the fluid, d_p is the diameter of catalyst particles, ρ is the density of fluid, D molecular diffusivity of the transferred component, ε void fraction of the catalyst bed, α and β are constants which must be determined experimentally. For gases for $3<Re<2000$ and $0416<\varepsilon<0.778$, $\alpha = 0.357$ and $\beta = 0.359$. For liquids for $55<Re<1500$ and $0.35<\varepsilon<0.75$, $\alpha = 0.250$ and $\beta = 0.310$.

The data on heat transfer are correlated in the same way as the data on mass transfer. For heat transfer phenomena the Prandtl number was defined:

$$Pr = \mu.C_p/k_{fld} \tag{58}$$

where C_p is the specific heat of the fluid, k_{fld} is the thermal conductivity of the fluid, μ is the viscosity of the fluid. Then for the j_H and heat transfer coefficient h we have the equations:

$$j_H = \frac{h}{C_p.G} \Pr^{2/3} = \frac{\alpha}{\varepsilon} \mathrm{Re}^{-\beta} \tag{59}$$

and

$$h = \frac{\alpha.\mathrm{Re}^{-\beta}.C_p^{1/3}.G.k_{fld}}{\varepsilon.\mu^{2/3}} = \frac{j_H.C_p^{1/3}.G.k_{fld}}{\mu^{2/3}} \tag{60}$$

Between the j_D and j_H factors there exists a correlation

$$j_H = 1.08.j_D \tag{61}$$

6.3. EXTERNAL DIFFUSION REGIME

In the external diffusion regime the reaction rate is determined by general diffusion laws, the value of the mass transfer coefficient of reactants and fluid dynamic parameters. Under steady state conditions the reaction rate will be equal to the diffusion rate:

$$k_c.(C_o - C_s) = k.C_s \tag{62}$$

The surface concentration c_s is equal to:

$$c_s = k_c.C_o/(k_c + k) \tag{63}$$

Then the reaction rate in external diffusion regime r_{ed} is given by the

$$r_{ed} = \frac{k.k_c}{k + k_c} C_o = \frac{1}{\frac{1}{k} + \frac{1}{k_c}} C_o = k_{eff}.C_o \tag{64}$$

The reverse value of the effective rate constant k_{eff} is equal to the sum of the kinetic (1/k) and diffusion ($1/k_c$) resistances. If $k_c >> k$ then $C_o \approx C_s$ and $k_{eff} \approx k$. In this case the reaction rate will be determined by the chemical reaction i.e. the reaction proceeds in the kinetic regime. If $k >> k_c$ then $C_s \approx 0$ and $k_{eff} \approx k_c$. In this case the reaction rate will be determined by the diffusion of the reactants to the catalyst surface i.e. the reaction proceeds in the external diffusion regime.

In the external diffusion regime all reactions proceed as first order reactions. It is characterised by existence of great temperature difference between the catalyst surface and reaction mixture. Changes in the catalytic activity of the catalyst do not influence the reaction rate. Reaction rate depends on the linear flow rate or mixing and on the catalyst particle size. The effective activation energy under these conditions is equal to the activation energy of molecular diffusion 4.2 - 12.5 kJ/mol.

6.3.1. Influence of different factors on the reaction rate in external diffusion regime

(i) Temperature - The reaction rate in external diffusion regime is proportional to the temperature. This dependence is determined by the temperature dependence of the diffusion coefficient of reactants. Therefore increasing the reaction temperature leads to transition from kinetic to the external diffusion regime and vice versa. Due to the low velocity of the heat transfer process, a large increase in the catalyst temperature can be observed which can lead under steady state conditions to the appearance of an autothermal regime.

(ii) Pressure - The diffusion coefficient increases with the decrease of the pressure, which leads to increase of the reaction rate in the external diffusion regime. However pressure has influence on other process parameters like linear velocity and in general the dependence becomes more complicated.

(iii) Flow rate - The increasing of the flow rate leads to the increasing of the mass transfer processes and therefore it helps to transfer the system into the kinetic regime.

(iv) Mixing - By increasing the intensity of mixing the fluid flow becomes more turbulent and decreases the thickness of the boundary laminar layer. This means that the reaction rate is increased and under certain mixing conditions it is possible that the external diffusion influence becomes negligible.

(v) Catalyst particle size - The smaller the catalyst particle size is, the higher is the diffusion rate and therefore the higher is the reaction rate.

(vi) Catalyst particle porosity - The porosity has no influence on the reaction rate in the external diffusion regime.

(vii) Catalyst activity - In the external diffusion regime the reaction rate is controlled be external diffusion process. Increasing the catalyst activity does not influence the overall reaction rate. Decreasing the catalyst activity will permit the system to enter the kinetic regime. Therefore if certain catalytic process proceed in the external diffusion regime the type and activity of the used catalyst do not play important role.

(viii) Catalyst selectivity - The transition from kinetic to the external diffusion regime can change the reaction selectivity in both consecutive and parallel type of reactions. This is due to the increased residence time of the reactants and products at the catalyst surface.

(ix) Catalyst poisoning and deactivation - The catalyst poisoning and deactivation do not exert any influence on the reaction rate in the external diffusion regime until the catalytic activity of the catalyst is decreased to such an extent that the system is transferred into the kinetic regime. Under these conditions it is possible that the rate of poisoning can be decreased due to slow diffusion to the catalyst surface.

6.3.2. Criteria for absence of the interphase transport limitations.

(i) Carberry criterion for the absence of interphase concentration gradients in isothermal systems at effectiveness factor $\eta \geq 0.95$ and first order reaction:

$$\frac{\eta . k}{k_m . A} \prec 0.1 \qquad \text{for } \eta \geq 0.95 \text{ and } n = 1 \qquad (65)$$

where k is the first-order rate constant per unit particle volume, k_m is the mass transfer coefficient between gas and particle, A is the external surface to volume ratio.

(ii) Mears criterion for the absence of interphase concentration gradients in isothermal systems at effectiveness factor η ≥ 0.95 and power-law kinetics:

$$\frac{r.R_p}{C_o.k_m} \prec \frac{0.15}{n} \tag{66}$$

(iii) Mears criterion for the absence of interphase temperature gradients in isothermal systems at effectiveness factor η ≥ 0.95 and power-law kinetics:

$$|\chi| = \frac{(-\Delta H).r.R_p}{h.T_o} \prec \frac{0.15R.T_o}{E} \tag{67}$$

where h is the heat transfer coefficient between gas and particle. The value of this criterion is independent of the fact whether intraparticle gradients exist or not.

(iv) Mears criterion for the absence of intraparticle and interphase gradients in isothermal systems for effectiveness factor η ≥ 0.95 and power law-kinetics

$$\frac{r.R_p^2}{C_o.D_{eff}} \prec \frac{1+0.33.\gamma.\chi}{|n-\gamma.\beta|(1+0.33.n.w)} \tag{68}$$

where C_o and T_o are the bulk concentration, temperature and

$$w = \frac{r.R_p}{C_o.k_m}, \quad \gamma = \frac{E}{R.T_o}, \quad \beta = \frac{-\Delta H.D_{eff}.C_o}{\lambda.T_o}$$

(v) Mears criterion for isothermal operation at effectiveness factor η ≥ 0.95, $|\gamma.\beta + 0.33n.\gamma.\chi| < 0.05.n$

6.4. HEAT AND MASS TRANSFER IN POROUS CATALYSTS

Heterogeneous catalytic reactions proceed on the surface of porous catalysts and therefore is accompanied by pore diffusion of the reactants and reaction products into and out of the catalyst grains and heat transfer process.

Pore diffusion may occur by one or more of three mechanisms: ordinary (molecular) diffusion, Knudsen diffusion and surface diffusion. The general characteristics of molecular diffusion were discussed in the previous section of this paper. We shall discuss shortly the general characteristics of Knudsen diffusion.

Knudsen diffusion is observed when the gas density is low or pores are quite small or in both cases. Under these conditions molecules collide with pore walls much more frequently than with one another. Knudsen diffusion is not observed in liquids. Kinetic theory provides following relation for Knudsen diffusion in gases in a straight round pore:

$$N = \frac{D_k}{RT} \cdot \frac{(p_1 - p_2)}{x_o} = \frac{2.r_e}{3RT}\left(\frac{8RT}{\pi M}\right)^{1/2} \frac{(p_1 - p_2)}{x_0} \qquad (69)$$

where D_k is the Knudsen diffusion coefficient

$$D_k = 9700.r_e\sqrt{\frac{T}{M}} \qquad (70)$$

r_e is the pore radius in cm, T is the absolute temperature, M is the molecular weight. Since the number of is molecular collisions are negligible each component in a reaction mixture behaves as though it is present alone.

The pore geometry of solid catalysts is poorly understood and empirical model must be used. For straight round pore with radius r_e has volume to surface ratio of $1/2.r_e$. If the porous material has a total surface S_g (cm^2/g) and average pellet density ρ_p (g/cm^3) for pore radius r_e we obtain:

$$r_e = \frac{2V_g}{S_g} = \frac{2\theta}{S_g.\rho_p} \qquad (71)$$

and the Knudsen diffusion coefficient for a porous solid become:

$$D_{K,eff} = \frac{D_K.\theta}{\tau_m} = 19400\frac{\theta^2}{3\tau_m.S_g.\rho_p}\sqrt{\frac{T}{M}} \qquad (72)$$

The void fraction θ has been introduced so that the flux given by $D_{K,eff}$ will be based on the total cross section of porous solid, not just the pore cross section. The tortuosity factor τ_m allows for both tortuous path and the effect of the varying cross section of individual pores.

In many cases the solid state contains pores with broad distribution by pore radius. It means that the diffusion in pores will proceed by both Knudsen and molecular diffusion. This regime is called transition. For the effective diffusion coefficient D_{eff} in the transition regime one can obtain the following equation:

$$\frac{1}{D_{eff}} = \frac{1}{D_{K,eff}} + \frac{1}{D_{12,eff}} \tag{73}$$

where $D_{12,eff}$ is the effective diffusion coefficient for molecular diffusion.

$$D_{12,eff} = D_{12}.\theta/\tau \tag{74}$$

6.5. INTERNAL DIFFUSION REGIME

In order to take into account the influence of pore diffusion on reaction rate the effectiveness factor η is introduced.

$$r = \eta.k.C_s^n \tag{75}$$

where $\eta = r_{obs}/r_{intr}$, r_{obs} is the observed reaction rate, r_{intr} is the intrinsic chemical reaction rate, C_s is the concentration at the particles surface, n is the reaction order. If η has value between 0.95 and 1 no internal diffusion resistance is taking place.

The theoretical treatment of the problem leads to the following expression for ηas a function of Thiele modulus ϕ:

$$\eta = \frac{1}{\phi}(\frac{1}{tgh3\phi} - \frac{1}{3\phi}) \tag{76}$$

The Thiele modulus is given by the formula:

$$\phi = R\sqrt{\frac{k.C_s^{n-1}}{D_{eff}}} \tag{77}$$

The Thiele modulus combines in one criterion the particle size R (representing the catalyst macrostructure), effective diffusion coefficient D_{eff} (representing the catalysts microstructure and porosity) and $k.C^{n-1}$ (representing the chemical reaction characteristics). The square of the Thiele modulus is the ratio between the characteristic times for transport $\tau_{diffusion}$ and reaction $\tau_{chemical\ reaction}$:

$$\phi^2 = (R^2/D_{eff}).k.C_s^{n-1} = \tau_{diffusion}/\tau_{chemical\ reaction} \tag{78}$$

The effective depth of the reaction H inside catalyst grains can be estimated by the formula:

$$H = \gamma.\sqrt{\frac{r}{C_s.D_{eff}}} \tag{79}$$

where γ is constant with the value near to unity.

6.6. INFLUENCE OF DIFFERENT FACTORS ON THE REACTION RATE IN THE INTERNAL DIFFUSION REGIME

(i) Temperature - The temperature dependence in the internal diffusion regime is not so strong compared to that in the kinetic regime. A catalyst operating at a low effectiveness factor will show apparent activation energy on an Arrhenius plot that is arithmetic mean of the activation energies for the diffusion process and for the chemical reaction.

$$E_{obs} = 0.5.(E + E_D) \tag{80}$$

(ii) Temperature regime - The temperature gradients within catalyst pellet in the internal diffusion regime are in general more favourable than in the kinetic regime. The pellets during processes accompanied with high heat effect and high activation energy are highly nonisothermal. This circumstance can lead to compensation of diffusion retardation and the reaction rate in diffusion regime can be larger then in the kinetic regime. Increasing the reaction temperature leads to transition from kinetic to the internal diffusion regime and vice versa.

(iii) Pressure - High-pressure increase the probability of transition from Knudsen diffusion to molecular diffusion. At the same time the molecular diffusion coefficient decreases with pressure increase. The pressure influence depends upon the form of kinetic equation used to describe the reaction rate dependence on the pressure. In general the pressure influence can not be beforehand predicted in advance.

(iv) Flow rate - Low flow rates help the transition from internal diffusion to kinetic regime.

(v) Catalyst particle size - Decreasing particle size permits larger part of the grain to participate in the reaction. When the entire internal surface becomes accessible to reactant molecules a transition into the kinetic regime is accomplished.

(vi) Catalyst porosity - Reaction rate must be increased with increasing the catalyst porosity since both Knudsen and molecular diffusion coefficients increase in larger pores.

(vii) Reaction rate - The reaction rate in diffusion regime is smaller than the reaction rate in kinetic regime. The higher the reaction order is the stronger is the influence of the internal diffusion. At high degrees of conversion the transition to kinetic regime becomes more probable.

(viii) Diffusion disguise of selectivity - When diffusion resistance exists inside a catalyst particle, the selectivity may change depending on the type of reaction occurring. Three types of selectivity shall be treated:

(a) Selectivity Type I

$$\begin{array}{ll} 1)\ A = B + C & \text{(desired)} \\ 2)\ X = Y + Z & \text{(undesired)} \end{array} \tag{81}$$

An example of this type of reaction is the hydrogenation of olefins in gasoline where it is undesirable to hydrogenate the aromatics. In the absence of diffusion limitation exists the selectivity is defined as follows

$$S_o = \frac{r_1}{r_2} = \frac{k_1 . C_a}{k_2 . C_x} \tag{82}$$

In the presence of diffusion limitations we can write:

$$S_d = \frac{r_1}{r_2} = \frac{\eta_q . k_1 . C_a}{\eta_2 . k_2 . C_x} = \frac{\eta_1}{\eta_2} S_o \tag{83}$$

In the limiting case $\phi > 3$ and we can write $\phi = R(K_i/D_i)^{1/2} = 1/\eta$. Usually $D_1 = D_2$ and (83) is transformed into:

$$S_d = (K_2/K_1)^{1/2} . S_o \tag{84}$$

The intrinsic selectivity is reduced by the diffusion limitation and efforts should be made to either decrease particle size or increase pore diameter of the catalyst in order to assure transfer to the kinetic regime.

(b) Selectivity Type II

1) A = B (desired) (85)
2) A = C (undesired)

Such a set of reactions can represent the oxidation of ethylene both to ethylene oxide and to undesired CO_2 and water. Since A reacts simultaneously to both B and C no diffusion limitations will appear in the selectivity behaviour. The diffusion of A however can reduce the overall activity. If reactions 1) and 2) are not of the same order, a diffusion effect may occur. If there are no diffusion limitations

$$S_o = \frac{r_1}{r_2} = \frac{k_1}{k_2} C_{Ao}^{n-m} \tag{86}$$

If diffusion limitation is present

$$S_d = \frac{r_1}{r_2} = \frac{k_1}{k_2} C_A^{n-m} \tag{87}$$

Since due to diffusion C_{Ao} will always be greater than C_A it is clear that when n is greater then m then the diffusion will reduce the selectivity. If m is greater than n, the diffusion will enhance the reaction selectivity.

(c) Selectivity Type III

$$A \rightarrow B \rightarrow C \tag{88}$$

Example for such set of reaction is catalytic cracking where A is the feedstock, B is the gasoline and C are the lighter products. Without diffusion limitations the selectivity of this reaction towards the product B is given below:

$$S_o = -\frac{r_B}{r_A} = 1 - \frac{k_2 . C_B}{k_1 . C_{Ao}} \tag{89}$$

With diffusion limitations the selectivity of the process is

$$S_d = -\frac{r_B}{r_A} = 1 - \frac{k_2 . C_B}{k_1 . C_A} \tag{90}$$

By plotting the conversion of A to B versus the total conversion of A for different values of Thiele modulus one obtain a family of curves passing through maximum. These results show that an optimal selectivity toward B can be obtained via changing the porous structure of the catalyst.

6.6.1. Criteria for absence of intraparticle diffusion limitations

(i) Weisz and Prater criterion for isothermal spherical particle at effectiveness factor $\eta \geq 0.95$

$$\frac{r . R_p^2}{C_o . D_{eff}} \prec \psi \text{ : for n = 0, } \psi = 6\text{; for n=1; } \psi = 1\text{; for n=2, } \psi = 0.3; \tag{91}$$

where r is the reaction rate per unit catalyst particle volume, R_p is the catalyst particle diameter, C_o is the reagent concentration at the catalyst surface, D_{eff} is the effective diffusion coefficient of the reagent within the catalyst particle. The value of ψ depends on the reaction order in the following way $\psi = 6$ for a zero order reaction; $\psi = 1$ for a first order reaction; $\psi = 0.3$ for a second order reaction.

(ii) Hudgins' criterion for isothermal spherical particle at effectiveness factor $\eta \geq 0.95$

$$\frac{r . R_p^2}{C_o . D_{eff}} \prec \frac{1}{|n|} \tag{92}$$

where n is a positive reaction order different from zero.

(iii) Anderson’s criterion for absence of temperature gradients at effectiveness factor $\eta \geq 0.95$

$$\frac{|\Delta H|.r.R_p^2}{\lambda.F_o} \prec \frac{T_o.R}{E} \tag{93}$$

where ΔH is the heat of reaction, r is the reaction rate per unit catalyst particle volume, R_p is the particle diameter, F_o is the molal feed flow rate, λ is the catalyst effective thermal conductivity, T_o is the temperature of the catalyst surface, R is the gas constant, E is the true activation energy.

(iv) Kubota and Yamanaka criterion for the absence of temperature and concentration gradients at effectiveness factor $\eta \geq 0.95$

$$\frac{r.R_p^2}{C_o.D_{eff}} \prec \frac{1}{|n-\gamma.\beta|} \quad \eta \geq 0.95 \tag{94}$$

where

$$\gamma = \frac{E}{R.T_o}, \text{ and } \beta = \frac{-\Delta H.D_{eff}.C_o}{\lambda.T_o}$$

(v) Mears and Petersen criterion for the absence of temperature and concentration gradients at effectiveness factor $\eta \geq 0.95$

$$\frac{r.R_p^2}{C_o.D_{eff}} \prec a \tag{95}$$

If the reaction order is $n \approx \gamma\delta$ then a = 13

6.7. DETERMINATION OF THE EFFECTIVE DIFFUSION COEFFICIENTS

Some elements of the theory of mass transfer phenomena and its influence on the proceeding of heterogeneous catalytic reactions presented in previous part of this paper show that the key point for the application of different theoretical approaches to catalytic practice is the knowledge of the effective diffusion coefficient values.

The simplest and most popular method is that of Wicke-Kallenbach [25]. The solid pellet is mounted in such a way that two opposite faces are exposed. One face is exposed to a stream of gas A, the other face is exposed to that of gas B. There should be no pressure difference between two sides of the pellet. The gas stream A is then analysed for concentration of B and from this information using the values of the pellet dimensions the effective diffusion coefficient D_{eff} [$cm^2.s^{-1}$] is calculated from the formula

$$D_{eff} = \frac{L}{S} F_A . C_B \tag{96}$$

where L is the thickness of the pellet in cm, S is the cross section of the pellet in cm^2, F_A is the flow rate of the gas stream A in $cm^3.s^{-1}$, C_B is the concentration of gas B in the stream A, expressed as a mol part.

The Wicke-Kallenbach method does not take into account the influence of the dead end pores. This disadvantage can be overcome by using dynamic methods for effective diffusion coefficient determination like dynamic Wicke-Kallenbach method or gas chromatographic method.

Study of the mass transfer characteristics of industrial copper catalysts for nitrobenzene hydrogenation and for low temperature water-gas shift reaction [26] had shown that the heat and mass transfer parameters are changing during the different steps of catalyst pre-treatment procedures and catalyst deactivation. The reduction of the catalysts decreases the tortuosity τ of the pores with about 50%. The values for τ are decreasing with increasing the temperature of measurements and at 433 K the obtained values of τ for both catalysts in both forms are two times smaller than at 293 K. For both catalysts, after reduction substantial increase in D_{eff} is observed. The higher measurement temperature is the larger is the difference between the D_{eff} for oxide and reduced forms. For both catalysts the difference estimated vary from 277 % at 293 K to 576 % at 533 K.

6.8. INTRAREACTOR CRITERIA FOR ABSENCE OF TRANSPORT LIMITATIONS

(i) Criterion for the control of bypassing effects due to dilution

$$\frac{L}{D_p} \succ 250 \frac{b}{\Delta} \tag{97}$$

where L is the reactor length, Dp is the particle diameter, b is the volumetric dilution ratio inert/catalyst, Δ is the relative experimental error in the degree of conversion.

(ii) Mears criterion for the absence of radial temperature gradients for high values (>100) of R_o/R_p ratio

$$\frac{\left|\Delta H\right| . r_b . R_0^2}{k_e . T_w} \prec 0.4 \frac{R . T_w}{E} \tag{98}$$

where r_b is the reaction rate per unit bed volume $r_b = (1-\varepsilon)/(1+b).r$, ε is the bed void fraction, k_e is the effective thermal conductivity of the catalyst bed, R_o is the reactor radius, T_w is the reactor wall temperature

(iii) Mears criterion for the absence of radial temperature gradients for low values of R_o/R_p ratio

$$\frac{\left|\Delta H\right|.r_b.R_0^2}{k_e.T_w} \prec 0.4\frac{R.T_w/E}{[1+16(R_p/R_o).Bi_h]} \tag{99}$$

where $Bi_h = h_w R_p/k_e$, h_w is the heat transfer coefficient between wall and the gas, R_p is the particle radius

(iv) Mears criterion for minimum reactor length required for freedom from significant axial dispersion effects for n^th^ order kinetics

$$\frac{L}{D_p} \succ \frac{20n}{Pe_a}\ln\frac{C_o}{C_f} \tag{100}$$

where n is the reaction rate order, C_o and C_f are the inlet and effluent concentrations of reactant, Pe_a is the axial Peclet number $Pe_a = v.D_p/D_a$, D_a is axial dispersion coefficient, *v* is the superficial fluid velocity.

7. Scale of units for catalytic activity testing

The units for the catalytic activity testing according to their scale can be divided to three groups. The scales of these groups and the tasks, which can be solved, are:

7.1. LABORATORY UNITS

The laboratory units are used for basic research studies and for preliminary tests of big number catalyst samples. The mass and heat transfer limitations are usually avoided. Typical laboratory unit consists of reactor, devises for regulation of gas and liquid flow, sampling devises and analytical instrument. It has no similarity with industrial units. Major parameters of the units are:

(i) Amount of catalyst - up to 100 g
(ii) Liquid Hourly Space Velocity (LHSV) - up to 50 cm^3/h
(iii) Gaseous Hourly Space Velocity (GHSV) - up to 0.10 m^3/h
(iv) Catalyst particle size - 0.1 - 1 mm
(v) Mass and heat transfer limitations - no
(vi) Price of the unit and experiments - - low

7.2. PILOT PLANT UNITS

The pilot plant units are used for testing of a small number of promising samples selected in laboratory tests. The mass and heat transfer limitations are not avoided. Typical pilot plant unit consist of elements some of which are characteristic for the industrial unit such as heat exchanger, product separation, reaction mixture circulation. Major parameters of the units are:

(i) Amount of catalyst - in the range of 1 to 10 kg
(ii) Liquid Hourly Space Velocity (LHSV) - in the range of 0.01 - 0.05 m^3/h
(iii) Gaseous Hourly Space Velocity (GHSV) - in the range of 0.5 - 25 m^3/h
(iv) Catalyst particle size - industrial size
(v) Mass and heat transfer limitations - present in some cases
(vi) Price of the unit and experiments – high.

7.3. EXPERIMENTAL INDUSTRIAL UNITS

The experimental industrial units are used for final test of already selected industrial catalysts. It contains all elements of industrial units. The only difference from real industrial units is its size. Data concerning the real catalyst performance, critical regimes, industrial hazard and the unit performance as a whole is obtained. Major parameters of the units are:

(i) Amount of catalyst - in the range of tones.
(ii) Liquid Hourly Space Velocity (LHSV) - in the range up to several m^3/h
(iii) Gaseous Hourly Space Velocity (GHSV) - in the range up to 10000 m^3/h
(iv) Catalyst particle size - industrial size
(v) Mass and heat transfer limitations - present in some cases
(vi) Price of the unit and experiments - extremely high

8. Criteria for catalytic activity

Most of the industrial catalytic processes proceed at steady state regimes over catalysts with constant catalytic activity. Processes included in this group are carried out over catalysts with long lifetime from several months to several years. Typical for these processes is that they proceed in well-established steady state conditions and catalytic activity of the catalysts is practically constant during the catalytic tests. In this cases no special precaution should be taken to avoid catalyst deactivation or poisoning and there is no need of special analytical methods and equipment.

Below we shall discuss the different criteria used to describe the catalytic activity and selectivity of the catalysts for catalytic processes operating at steady state conditions.

8.1. SENSITIVITY OF THE METHODS FOR CATALYST TESTING ON DEGREE OF CONVERSION

Reaction rate equation in general form is expressed by

$$r = k(T).f(C_0, x, a_i) \tag{101}$$

where k(T) is the rate constant, which is function of temperature, C_o is the initial reactant concentration, x is the degree of conversion, a_i are the adsorption coefficients of the reactants and products of the reaction. Under standard reaction conditions changes in catalyst activity cause the changes in the degree of conversion:

$$dx = \frac{\partial x}{\partial k} dk + \sum_{i=1}^{n} \frac{\partial x}{\partial a_i} da_i \tag{102}$$

The entities $\partial x/\partial k$ and $\partial x/\partial a_i$ are sensitivities of the measurements of catalyst activity [27]. For chemically similar catalysts $f(C_o, x, a_i)$ is the same and a_i = const and we have:

$$\frac{dx}{dk} = \frac{x.f(C_o, x, a_i)}{k.f(C_o, x, a_i) - k.x.\dfrac{df(C_o, x, a_i)}{dx}} \tag{103}$$

Since $1 \geq x \geq 0$ we have at the two limiting values: at x = 0 we have dx/dk = 0, at x = 1, r = 0 and dx/dk = 0. This mean that the dependence (dx/dk)/x will pass through maximum. It is easy to show that for first order reaction this maximum corresponds to x = 0.5. From this result two conclusions follow:

i) Sensitivity of activity measurement is inversely proportional to the catalyst activity, which means that for testing more active catalysts we need more precise measurements.

ii) A maximal sensitivity can be achieved at conversions around 50 %.

8.2. REACTION RATE

The absolute measure for catalytic activity is the reaction rate. Reaction rate is expressed by number of moles reacted per unit time in unit reaction space. In case of the heterogeneous catalytic reactions the catalyst surface can be regarded as reaction space. Therefore the reaction rate of heterogeneous catalytic reaction can be expressed by number of moles reacted per unit time on unit catalyst surface area. The catalyst surface area can be replaced by some related quantities like catalyst weight, catalyst volume, and number of active centres per unit area. For closed system we can write

$$r = \frac{1}{\Omega}\frac{dN_i}{dt} = \frac{V}{\Omega.}\frac{dC_i}{dt} = \frac{V.P_i^o}{\Omega.RT}\frac{dx}{dt} \tag{104}$$

where r is the reaction rate, N_i is the number of moles of reactant *i*, C_i is mole concentration of the reactant *i,* V is the volume of the closed system, Ω is the reaction space (catalyst surface area, catalyst weight, catalyst volume, number of active centres per unit area), P is partial pressure of reactant *i*, x is the degree of conversion.

For open system we have

$$r = \frac{dx}{d\left(\frac{W}{F}\right)} = \frac{F.dx}{W} = \frac{dC}{d\left(\frac{W}{F}\right)} = \frac{F.dC}{W} \tag{105}$$

where W/F is the contact time [volume/(volume/time)] = [time], F is the flow rate in moles per time, W is the amount or volume of the catalysts charged into reactor, x is degree of conversion, C concentration of reactant. One should have in mind that concentration in a flow system is determined from ratio of flow rate F and volumetric flow rate *v,* i.e. C = F/*v*=(moles/time)/(litters/time) = moles/litter

Since the reaction rate is a function of the reaction mixture composition one can compare reaction rates for different catalysts only if experiments are made with the same composition of the reaction mixture at the same degree of conversion. Experimentally this can be achieved only if several experiments for every catalyst are made. It is worth to mention that for the open system with reactor with ideal mixing one should compare the compositions at the reactor outlet, while for the open system plug flow reactor the composition at the reactor inlet should be taken into account.

For complex catalytic reactions measure of catalytic activity should be reaction rate on independent stoichiometric routes as defined before. The rate of the reaction on stoichiometric independent routes (which we can not measure experimentally) is calculated from the reaction rates for the individual reagents in the system (which can be measured directly during the experiment) using the equation:

$$r_i = \sum_{j=1}^{M_T} \left\| \mu_{i,j} \right\|^T R_j \tag{19}$$

where r_i is the reaction rate for ith reagent, i = 1,2,....,n is the number of the reagents in the system, Rj is the reaction rate along the stoichiometric linearly independent route j, j = 1,2,.....,M_T, $\left\| \mu_{i,j} \right\|^T$ is an element of transposed stoichiometric matrix. Each element $\left\| \mu_{i,j} \right\|^T$ of the stoichiometric matrix gives the stoichiometric coefficient of ith reagent in jth reaction independent route.

This means that for characterisation of the catalytic activity of the catalyst in complex reaction instead of one reaction rate we will use a vector which elements are reaction rates on each independent reaction route. In multiroute reaction system we have to calculate the selectivities on stoichiometric independent routes, which is expressed as a ratio of reaction rate on the selected route to the sum of reaction rates on all independent routes.

$$S_j = \frac{R_j}{\sum_{j=1}^{j=M_T} R_j} \tag{106}$$

The so-called turnover number is another definition of the reaction rate. The turnover number is equal to the number of molecules reacted on one active surface center per unit time. The number of active surface centres in industrial catalysts however can not be estimated very precisely which leads to the big errors in the estimated reaction rate. Therefore it is recommendable not to use the turnover number for characterisation of activity of industrial catalysts.

8.3. REACTION RATE CONSTANTS

Reaction rate equation in general form is expressed by

$$r = k(T).f(C_0, x, a_i) \tag{101}$$

where k(T) is the rate constant which is function of the temperature, C_o is the initial reactant concentration, x is the degree of conversion, a_i are the adsorption coefficients of the reactants and products of the reaction. If we compare the catalytic activity of two catalysts with similar chemical composition and prepared by similar technologies we can write:

$$\frac{r_1}{r_2} = \frac{k_1(T)}{k_2(T)} \tag{107}$$

From equations (33) and (34) one can see that the reaction rate constants are not a single parameters but are function of the rate constants of the elementary reactions included in the reaction mechanism. The same is valid for the activation energy. Therefore, the equation (107) holds true only if $f_1(C_o, x, a_i) = f_2(C_o, x, a_i)$, the rate constants $k_1(T)$ and $k_2(T)$ have the same dimensions and activation energies are nearly equal.

This criterion for assessment of the catalytic activity can be used mainly for quality control in catalyst production. It is very risky to use the rate constants as a criterion for assessment of catalytic activity of the catalysts with different catalyst composition without knowledge of the corresponding rate equation.

This statement can be illustrated by the following example [28]. Let carry out the same reaction A = B on two different catalysts with known kinetics

$r_1 = k_1 P_a^{0.5}$ and $r_2 = k_2 P_a^2$

where P_a is partial pressure of A, r_1 and r_2, k_1 and k_2 are the reaction rates and rate constants on catalyst 1 and 2 correspondingly. Let at P_a =100 atm. and the same composition of the reaction mixture, the reaction rates have the values r_1 = 0.01 mol.s$^-$

^{1}.cm^{-2} and r_2 = 0.1 mol.s^{-1}.cm^{-2} and k_1 = 10^{-3} mol.s^{-1}.atm$^{-0.5}$.cm^{-2}, k_2 = 10^{-5}mol.s^{-1}. atm^{-2}.cm^{-2}. According to the rates given above the second catalyst is 10 times more active than the first one.

In order to compare the two constants with different dimensions we have to transform the equations in dimensionless form. We introduce the new quantities

$$\rho_1 = r_1/r_o; \qquad \rho_2 = r_2/r_o; \qquad \pi = P_a/P_o;$$

where r_o = 1 mol.s^{-1}.cm^{-2}, P_o = 1 atm, and we have:

$$r_1 = \rho_1 r_o; \qquad r_2 = \rho_2 r_o; \qquad P_a = \pi P_o.$$

Finally we obtain

$$\rho_1 = \xi_1\pi^{0.5}, \qquad \text{where } \xi_1 = k_1P_o^{0.5}/r_o$$
$$\rho_2 = \xi_2\pi^2, \qquad \text{where } \xi_2 = k_2P_a^{2}/r_o$$

The values of the dimensionless rates and constants now have values ρ_1 = 0.01 and ρ_2 = 0.1 and $\xi_1 = 10^{-3}$ and $\xi_2 = 10^{-5}$ correspondingly. From values of these constants follows that the first catalyst is 100 times more active than the second one, while rates data gives the opposite ranking.

These example shows that the reaction rate constant can used properly in limited number of cases only after taking into account all limitations discussed before.

8.4. DEGREE OF CONVERSION

Degree of conversion at fixed temperature, initial composition of the reaction mixture and time for batch reactor or contact time W/F for flow reactor one of the most popular criteria for expressing the catalytic activity in relative units. Experimentally, the measurement of degree of conversion is very simple and it is very convenient criteria for quality control tests. The application of this criterion is connected with some difficulties and limitations:

(i) The degree of conversion is proportional to the amount of the catalyst charged in the reactor only for the gradientless reactors since the reaction rate is calculated by following equation:

$$r = \frac{F.\Delta x}{W} \tag{44}$$

For batch reactor the reaction rate is estimated by the equation

$$t = N_o\int_0^x \frac{dx}{r.W} \tag{42}$$

and for integral flow reactor by the equation

$$\frac{W}{F} = \int_0^x \frac{dx}{r} \tag{43}$$

From eqns. (42) and (43) follows that in batch and integral flow reactors the degree of conversion is proportional to the amount of used catalyst only for zero order reaction. The absence of proportionality between observed degree of conversion means that experimentally we obtain characteristic value for this particular amount of catalyst, which is used, but it can not be used for characterisation of different catalyst charge.

(ii) From equation, (8), (33) and (34) follows that obtained degrees of conversion for two catalysts can be compared only if the functions $f_1(C_o, x, a_i)$ and $f_2(C_o, x, a_i)$ are identical.

Selectivity should be referred to the key reagents corresponding to every independent route. It is calculated as a ratio between measured degree of conversion for a given key reagent and the sum of degree of conversion of all key reagents.

$$S_j = \frac{X_j}{\sum_{j=1}^{j=M_T} X_j} \tag{108}$$

8.5. TIME (CONTACT TIME) NECESSARY TO ACCOMPLISH FIXED DEGREE OF CONVERSION

For two catalysts which obey the same reaction kinetics we can write:

$$\frac{k_1}{k_2} = \frac{t_2^x}{t_1^x} \tag{109}$$

where t^x_i is the time for batch reactors or contact time W/F for flow systems at which fixed degree of conversion for i^{-th} catalyst is obtained. The ratio (109) do not depend on the selected degree of conversion.

For this method hold true the same limitations as for the method based on comparison of rate constants discussed above.

8.6. TEMPERATURES NECESSARY TO ACCOMPLISH FIXED DEGREE OF CONVERSION

It is quite difficult to establish the beginning and the end of the reaction. Following the discussion about sensitivity of activity tests it is advisable to use degrees of conversion around 50 %. However in order to avoid mistakes due to different x-T dependence the best solution is to build the full curve and to use at least three characteristic temperatures. Usually this is done by using TPR technique. The disadvantage of this method is that the shape and position of x-T curves strongly depend on activation energy, reactants flow rates and the amount of catalyst used. This disadvantage can be avoided by replacing the degree of conversion with reaction rate.

This method has the advantage that it corresponds to the usual industrial practice. In order to keep the catalyst performance on the same level during the industrial run and compensate the activity loss due to catalyst deactivation, usually the reaction temperature is steadily increased.

8.7. ACTIVATION ENERGY

This method is based of comparison of activation energies on different catalysts. Taking into account the eqns. (33) and (34) and following discussion it is obvious that this comparison is justified only in the case when reaction kinetics for different catalysts we have exactly the same reaction kinetics. The application of this method is connected with many conditions, which make it not suitable for the application in industry.

8.8. REACTION TEMPERATURES FOR OBTAINING PRODUCT WITH PRELIMINARY FIXED QUALITY

This criterion is used mainly in oil processing industry. For example activity of the catalysts for catalytic cracking can be assessed by using Octane number of produced gasoline as a criterion.

9. Catalytic processes under non-steady state regime

For catalytic processes proceeding under non-steady state regime and constant temperature over catalyst with changeable catalytic activity the full kinetic model of given catalytic process should consists of the following of autonomous differential equations:

$$\mathbf{r} = \|\mathbf{A}\|_c . f(\mathbf{c}, \mathbf{x}, \alpha, T) \tag{110}$$

$$d\mathbf{x}/dt = \|\mathbf{A}\|_x . f_1(\mathbf{c}, \mathbf{x}, \alpha, T) \tag{111}$$

$$d\alpha/dt = f_2(\mathbf{c}, \mathbf{x}, \alpha, T) \tag{112}$$

where $\|\mathbf{A}\|_c$ and $\|\mathbf{A}\|_x$. are stoichiometric matrixes for reagents and ISC, **c** is a vector of reagents concentrations, **x** is a vector of ISC concentrations, α characterises the catalyst surface state and composition, T is the reaction temperature. If catalyst activity is constant then dα/dt = 0. At constant temperature equation (110) describes the dependence of reaction rate on the changes of reagent concentrations **c**, on the changes of the concentrations of ISC **x** and on the changes of the state of catalyst α, equation (111) describes the changes of the concentrations of ISC with astronomical time as a function of **c, x,** and α, and equation (112) describes the changes of state of the catalyst with astronomical time as a function of **c, x,** α. The solution of the eqns. (110), (111) and (112) will describe the behaviour of the catalyst in non-steady state.

From point of view of the reaction mechanism, in general, the measured reaction rate at non-steady state conditions should be equal to the rate of some of the elementary steps, which are different from the limiting reaction steps at steady state regime. The reasons for the deviation from steady state regimes are numerous: presence of redox cycle in catalyst surface, presence a non-linear elementary steps in the reaction mechanism, changes of reaction mechanism due to changes of the degree of conversion, catalyst re-crystallisation, deactivation, catalyst poisoning, etc. Most of these factors acts spontaneously and are part of the properties of the system catalyst-reaction media and as a result different phenomena are observed like multiple steady states, oscillating reactions, chaotic behaviour, heat explosion etc.

Development of kinetic models of non-stationary catalytic processes is a difficult task. These models should account for the following factors: the rates of the elementary chemical transformations, the rates of changing of reactant composition, the rates of changing of the activity of the catalyst, diffusion of the reacting species in the catalyst pores, and etc. The investigation of the dynamics of the catalytic process i.e. the evolution of the heterogeneous catalytic reactions gives the information which is used for the studies and development of the dynamics and stability of the catalytic reactors, which in their turn determine the optimal starting, transition and operation regimes.

In limited number of cases some catalytic processes are realised in industry using nonsteady state technologies [29].

9.1. NONSTEADY STATE METHODS FOR CATALYST TESTING

Nonsteady state methods for catalyst testing play an important role especially for evaluation of catalysts working at nonsteady state conditions like catalysts for cleaning of the exhausted gases from motor vehicles and for study of the reaction mechanisms.

By intentional deviation of different reaction parameters from steady state regime we are able to study the reaction rates of different elementary steps of the reaction. If changes in the reaction parameters have the same time scale as the time scale of the steps of the catalytic process the reaction proceeds in nonsteady regime. In Table 1 are given the relaxation time in seconds for different steps of catalytic processes.

Table 1. Relaxation time for different steps of catalytic processes

Step	Relaxation time, s
Chemical steps	$10^{-2} – 10$
Steps modifying catalysts	$10^{-2} – 10^{6}$
Diffusion in catalyst grain	$10^{-2} – 10$
Mass transfer to the catalyst outer surface	$10^{-1} – 10^{2}$
Heat transfer	$10^{-1} – 10^{2}$
Flow hydrodynamics	$10^{-3} – 10^{-1}$

Most frequently used methods for creation of deviations from the steady state regime are: (i) temperature programmed changes, (ii) pulsed reagents flow rate, (iii) changes in the reagents composition at the reactor inlet and (iv) fast deactivation or poisoning of the catalyst.

The characteristic features of nonsteady state methods for catalyst testing are:

Basic principle - differential or integral reactor
Main requirement - plug flow or ideal mixing
Basic condition - non-steady state regime
Typical gradients – temperature, concentration and other gradients by time and along the catalyst bed
Advantages - measurement of reaction rate of the elementary steps
Disadvantages - complicated equipment and treatment of experimental data

10. Accelerated testing of catalytic properties of heterogeneous catalysts

The accelerated catalyst design is a new and very dynamic development in the area of applied catalysis. It is of special interest for industry since it can help shorten substantially the time for development of new catalyst.

The catalyst manufacture requires a large volume of scientific research work. It is one of the most complicated chemical productions, which demands a direct and continuous control. Its development is directly dependent on the state of basic research and applied studies in the field of catalysis, which in their turn demand considerable funding. For instance the elaboration of an effective catalyst for the cleaning of exhaust gases from gasoline engines with internal combustion costed about 2 billion dollars to the General Motors company, where upon almost one thousand specialists have participated in this project [30]. The Davison Co., which is one of the leading producers of catalysts for fluid-bed catalytic cracking (FCC) has developed the new catalysts of the XP series, designed for cracking of heavy oil residuals, in the course of 10 years.

The catalyst manufacture is distinguished by its dynamics. In the rates of its development this branch overtakes considerably the development of the other branches of the chemical, petrochemical and oil processing industry. Due to the fact that the effectiveness of a given catalytic production is determined to a great extent by the operation of the catalytic unit an incessant work is going on the development and production of new and more effective catalysts. On the average 15-20% of all used catalysts are replaced annually with newer types. The special attention is paid especially to those catalysts, which are used, for the production of new articles and novel processes, based on new types of raw materials.

A specific feature of the catalyst business is that the economic results of the production of new types of catalysts lags behind those in the industry, where they are being used with about 8 - 10 months on the average.

The dynamic development of the industrial catalysis puts on the agenda the problem to increase essentially the rate of kinetic model construction and accelerated testing of catalytic activity. The solving of this problem is unthinkable without applying the recent achievements catalysis science, reactor design, theory of the design of optimal experiment, the use of automated systems for carrying out the kinetic experiments and data acquisition on the basis of modern computers during all stages of obtaining and processing the experimental data. Several approaches for the development of the accelerated tests for measurement of the catalytic activity can be used:

(i) Development of new types catalytic reactors

(ii) Development of the new methods for testing of catalyst activity

(iii) Application of new very fast analytical methods for reagents concentration measurements

(iv) Development and application of new methods for experimental design in planing of the testing experiments.

(v) Development of new effective mathematical methods for treatment of experimental data.

10.1. DEVELOPMENT OF NEW TYPES CATALYTIC REACTORS

In recent review [31] different new ideas and developments for process intensification are discussed. The process intensification is a strategy for dramatic reduction in the physical size of the reactors while achieving given production objectives. Main idea is creating multifunctional reactive system (catalysts, reactors etc.), which allows several functions (processes) to occur simultaneously i.e. to combine the chemical reaction with momentum, heat and mass transport in a single vessel. The innovation of catalytic reactors is the heart of such process technologies. Below we shall discuss very short some of these new developments.

10.1.1. *Multichannel reactors*

In order to be able to analyse big libraries containing thousands of catalyst compositions different types of multichannel reactors has been constructed and used [32-35]. The numbers of channels in such reactors vary from 8 to 80 channels. Some characteristic features of multichannel reactors are given below:

Basic principle - integral reactor
Main requirement - ideal plug flow
Basic condition - steady state
Typical gradients - radial and longitudinal gradients of concentration and temperature, the catalyst bypassing, channelling near the reactor wall.
Advantages - similarity to industrial units, many small samples can be tested in a short time, decrease the time of screening
Disadvantages - difficulties in achieving quasi steady state, no direct measurement of the reaction rate, many gradients, complicated sampling and analytical devises. For big number of channels is difficult to establish the same space velocity for every channel because of different resistance of the catalyst layers. It is difficult to perform different pre-treatment regimes in case of samples with different chemical nature. Therefore it is impossible to vary the catalyst composition in very broad intervals. If catalysts have different composition and activity the temperature regime in different tubes will be different, which will increase the experimental errors and decrease the opportunity to distinguish between good and bad samples. This type of reactors are not suitable for studying complex catalytic reactions because of difficulties to perform fast and proper analysis of reaction products. Nevertheless, multichannel reactors can give very good

results if the researcher takes into account all above-mentioned disadvantages and interpret the obtained results properly.

Multichannel reactors can work in different modes: (i) all channels in parallel or (ii) consecutively every single tube. In both modes big number of experimental difficulties arise connected with establishing of steady state regime, sampling technique, analytical methods and procedures, and etc. Probably, the crucial problem is the selection of appropriate analytical method.

Multichannel reactors are intended for use mainly in the process of screening of big number samples (big library) in order to select the promising composition, which have to be studied in details by traditional methods. Multichannel reactors are already offered commercially on the market by some companies [35].

10.1.2. *Miniature reactors*

New direction in the design of laboratory catalytic reactors is introduction of microreactors with size of several millimetres connected with analytical devises so-called "lab-on-a-chip [36-37]. Microreactors allows substantial improvements of the heat and mass transfer conditions, as well as of the catalyst performance and especially of the selectivity. Application of appropriate fast, precise, reliable and applicable for very small quantity of chemicals analytical systems is the rate-limiting step in the most of the cases of real putting into practice of this technique. This type of miniaturisation has big potential for future improvements.

10.1.3. Pulse mass analyser

The pulse mass analyser is real time microbalance in a packed bed microreactor containing about 0.1 g catalyst sample [38]. It is based on the new method for measuring mass changes by monitoring frequency changes of a tapered element in a fixed bed reactor while reaction gases are passed through the sample. It is suitable for adsorption desorption measurements and catalyst deactivation studies. Mass transients of 0.1 sec can be reliability monitored.

10.2. ACCELERATED METHOD FOR CATALYST LIFETIME ESTIMATION

The most time consuming step during the design and development of industrial catalysts and the quality-checking procedures is estimation and catalysts lifetime. The express method for one-day laboratory test is proposed for prognosis of the activities and lifetime of the catalyst for several industrial processes gas phase hydrogenation of nitrobenzene to aniline, gas phase crotonealdehyde hydrogenation to butanol, liquid phase hydrogenation of crotonealdehyde to butiraldehyde, liquid phase gasoline sweetening process. [39-41].

The method is based on the knowledge of the deactivation behaviour of the catalysts under different reaction conditions, including extreme conditions of very high LHSV, and permits to predict the industrial lifetime and performance using the data obtained from one-day test in laboratory conditions.

It is well known fact that at different LHSV lifetime of the catalyst is different. On Fig. 1 the dependency life time/LHSV for different catalyst for aniline production is presented. The curve LHSV/lifetime is individual property of given catalyst. It has reproducible shape characteristic for any single catalyst, which have to be established experimentally. Any point from LHSV/lifetime curve can be used for lifetime estimation. It is clear, however, that the aim of express lifetime estimation is to obtain reliable result for as short as possible period of time which means that very high LHSV have to be used. At these conditions serious problems with heat and mass transfer might appear.

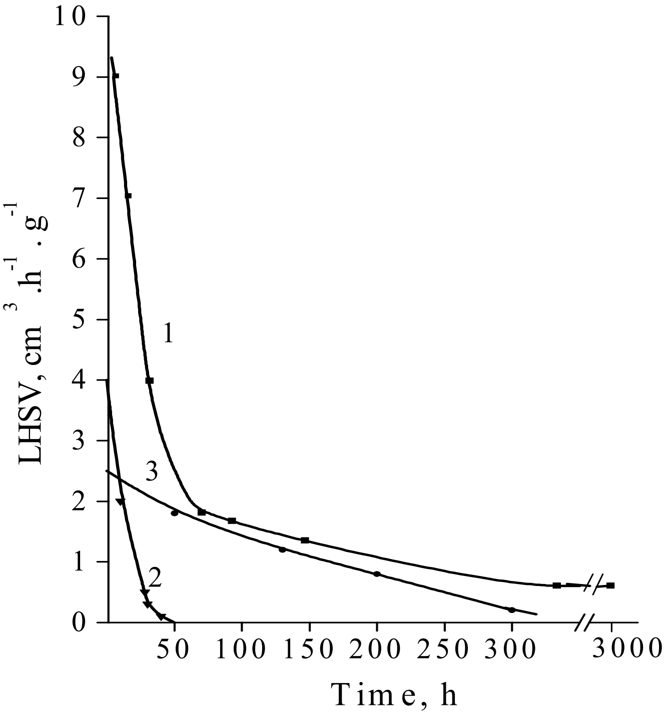

Fig.1. Dependence LHSV/catalyst lifetime for copper catalyst
for gas phase hydrogenation of nitrobenzene to aniline

The curve LHSV/lifetime for a given catalyst is prepared using data collected from different reactors. All experimental points are arranged well along the same curve. Below are presented the processes and catalysts for which the proposed method has been applied.

1. Process of gas phase hydrogenation of nitrobenzene to aniline. Used catalyst was kieselguhr-supported copper catalysts produced by Neftochim AD. Data from the following reactors were used: (i) Laboratory glass reactor containing 1 g catalyst with grain size 0.1 mm, (ii) Hungarian made pilot system OL-105/01 containing 5 g catalyst with grain size 1 mm, (iii) Pilot plant reactor containing 2 kg industrial pellets with size 6x6, (iv) Pilot plant reactor containing 20 kg industrial pellets with size 6x6, (vi) Industrial unit for aniline production with four packed bed reactors arranged in series. Each reactor contains 4000 kg catalyst with pellet size 6x6.

2. Process of gas phase crotonealdehyde hydrogenation to butanol. Used catalyst was kieselguhr-supported copper catalyst produced by Neftochim AD. The data from the following reactors were used: (i) Laboratory glass reactor containing 1 g catalyst with grain size 0.1 mm, (ii) Hungarian made pilot system OL-105/01 containing 5g catalyst with grain size 1 mm, (iii) Industrial unit for butanol production with four tubular reactors arranged in parallel. Each reactor contains 4000 kg catalyst with pellet size 6x6.

3. Liquid phase hydrogenation of crotonealdehyde to butiraldehyde. Used catalyst was alumina supported nickel catalyst produced by Neftochim AD. The data from the following reactors were used: (i) Laboratory liquid phase glass reactor containing 1g catalyst with grain size 0.01 mm, (ii) Industrial unit for butyraldehyde production with four liquid phase reactors arranged in parallel. Each reactor contains 150 kg powder catalyst with particle size 0.01mm.

4. Liquid phase gasoline sweetening process. Used catalyst was phtalocyanine catalyst produced in Neftochim AD. The data from following reactors were used: (i) Laboratory trickle-bed liquid phase metal reactor containing 1 g catalyst with grain size 0.6-1 mm, (ii) Pilot plant trickle-bed reactor containing 5 kg catalyst with particle size 0.5-2 mm and 8 atm. working pressure.

As illustration on Fig.1 curve 1 the data from estimation of lifetime of copper catalyst for gas phase nitrobenzene to aniline hydrogenation. At industrial conditions nitrobenzene LHSV = 0.5 $cm^3h^{-1}g^{-1}$ and temperature of 170 ^oC and H_2 to nitrobenzene molal ratio 1: 15 the lifetime of the catalyst for aniline production is about 3000 h (Curve 1). If we perform the catalytic activity test at much higher nitrobenzene LHSV i.e. 8 $cm^3h^{-1}g^{-1}$, the catalyst lifetime will be only 7 h, which means that one-day test can predict the catalyst lifetime.

The efficiency of the proposed method was tested and elaborated in different industrial units for catalysts production and for catalysts exploitation.

10.3 NEW METHODS FOR TREATMENT OF EXPERIMENTAL DATA

10.3.1. Application of new methods for treatment of experimental data

Experimental sequential design for planning kinetic experiments has a big potential to accelerate kinetic experiments and experiments of catalyst testing, but due to some experimental difficulties until now has not found wide application. In our paper [42] we had presented a critical evaluation of the difficulties in application of this method in laboratory practice. In the same time new approaches for treatment of experimental data from kinetic measurements and catalytic activity tests and description of computer programs are given.

10.3.2. Treatment of joint effects of diffusion resistance and catalyst deactivation on the catalyst activity and selectivity of complex reactions

New theoretical method for treatment of joint effects of diffusion resistance and catalyst deactivation on the catalyst activity and selectivity of complex reactions is proposed.

As a rule when catalytic reaction take place, precautions are taken to avoid the diffusion restriction, since it is generally accepted that their effect is disadvantageous for the target yield. However, the situation is not so evident in regard of processes subject to catalyst deactivation. When the process is accompanied by catalyst deactivation, effects evoked may be quite different. Depending on the mechanism peculiarities, the influence of diffusion may either increase or reduce the effect of deactivation. General analysis of the joint effect of the catalyst deactivation and intraparticle diffusion resistance on the proceeding of the heterogeneous catalytic reactions have shown that in certain cases the intraparticle resistance in the course of catalyst deactivation can have beneficial effect on the catalyst performance. This result was experimentally verified for the process of dehydrogenation of isopentene to isoprene over mixed oxide catalyst [43,44].

11. Discussion

The selection of optimum active substance does not mean that an optimum industrial catalyst has already been created. Undoubtedly, chemical composition is the main factor that determines the catalytic properties. However, even for one and the same chemical composition, depending on conditions and method of preparation, the catalytic properties of the catalyst may vary within a considerable interval. This is a consequence of changes in the nature of interaction between catalyst components, catalyst dispersion, porous and crystal structure, and other factors that have an essential influence on the catalytic reactions. In many cases the physicomechanical factors may prove to be decisive to select a certain catalyst production technology and a given type of catalysts.

The catalytic properties of a given catalyst with respect to its application in a certain industrial process are evaluated on the basis of the following criteria: (i) catalytic properties (catalytic activity and selectivity); (ii) chemical properties of the solid catalyst; (iii) surface properties of the solid catalyst; (iv) bulk properties of the solid catalytic material; (v) physical properties of the catalyst grain; (vi) mechanical properties of the catalyst grain, (vii) morphological properties of the catalyst grain.

Therefore, a great number of methods have to be used for catalyst characterisation. The primary purpose of catalyst characterisation is to provide information about catalyst properties and their relation to industrial catalysts performance. Catalyst characterisation is a very important element of the process of catalyst development, catalyst production, and catalyst application. Different users of catalyst characterisation results, like R&D teams, catalyst producers, catalyst users, and dealers have different aims and need different information to be supplied which correspondingly require the application of different methods and approaches to data acquisition. Some specific problems related to evaluation of results from catalyst characterisation are discussed below.

(i) Due to the complexity of the catalytic phenomena it is impossible to obtain sufficient and reliable information about reaction mechanism or catalyst structure and properties using any single method. In catalyst research practice it is a widely accepted approach that in order to attain deep insight into studied problem one should use as much modern methods as possible. For different catalytic processes different factors are playing important role and as a consequence of this circumstance different methods should play dominant role in the catalyst characterisation.

(ii) In general the catalyst should be regarded as an inseparable part of the larger system consisting of the reaction medium and the catalyst itself. Heterogeneous catalysts are very complex systems with pre-programmed properties. Some of these properties do not depend very much on the conditions under which they were measured. However, in many cases the situation is different. During the course of catalyst operation in industrial reactors at high temperature and pressure, under the influence of the reaction media and other factors the catalyst structure, composition and properties are changing. In some cases these changes are small, but sometimes they are quite substantial. For this reason it is very important to obtain information about the occurring processes not only from static measurements before and after catalyst use but also to follow all processes in their continuous development in the course of the catalytic process by carrying out ‘in situ’ studies. Unfortunately that is possible only in limited number of cases. Nevertheless ‘in situ’ studies of catalysts are indispensable and if possible this approach must be applied.

(iii) During the last decades due to the development of new theoretical approaches and computer technology we are witnesses of the revolutionary changes in the theoretical and experimental research methods of surface science, solid states physics and chemistry. The introduction of these new very powerful methods into catalysis research practice is changing the traditional manner of catalytic research. One should also bear in mind that although surface science techniques are very powerful and informative; all experiments are performed under conditions that are very far from those under which the real catalysis is taking place. Thus, the use of results from surface science measurements for description of the processes taking place under conditions of real catalysis should be performed always with precaution.

(iv) All traditional analytical methods and equipment have undergone dramatic changes due to introduction of computer technology. The reliability, speed of analysis and preciseness of the equipment has increased with orders of magnitude.

(v) Most of newly introduced instruments, especially those used for surface science measurements, are very expensive. A well-equipped laboratory for catalyst characterisation costs many millions of dollars, therefore, investments to organise a new laboratory or enlarge an existing one should be made carefully, accounting for both scientific and financial considerations.

The precise determination of catalytic activity, selectivity and lifetime of an industrial catalyst for a certain catalytic process is a very difficult, expensive and time-consuming task. In the first instance it is very important do define clearly the aim of these experiments and the information one needs. Two extreme cases in this sense are experimental data acquisition to elaborate an adequate kinetic model of the process or quality control tests in catalyst producer facilities. Not less important is the problem of testing experiments scale. First of all, the choice of scale can be made following technological expediency but also one should take into account that large-scale experiments are very expensive and time consuming.

The most common problems that one could encounter during catalytic tests of industrial catalysts are the following.

(i) Thorough testing of catalyst activity is expensive and time consuming and should be done with catalysts that have already passed other chemical, physical, mechanical and physicochemical tests.

(ii) Catalytic activity measurements provide reliable data if laboratory catalytic reactors are properly selected according to specific process and catalysts under study.

(iii) Heat and mass transfer processes always accompany heterogeneous catalytic reactions. It is very important to properly evaluate the heat and mass transfer effect on a catalytic reaction.

(iv) It is essential that the analytical methods and equipment used to analyse reaction mixture compositions at the reactor inlet and outlet are precise, fast, and reliable.

(v) Interpretation of catalytic activity measurements should always be related to results from other characterisation techniques: chemical, physical, morphological and mechanical. In this sense it is very important to combine catalytic activity measurements with ‘in situ’ studies by some physical methods to gain information about catalyst changes during catalytic runs.

11. Conclusions

1. The reaction rate is the only precise and reliable measure for the catalytic activity. All other methods for assessment of catalytic activity have limited applications and can be used only when all precautions are taken into account in order to avoid ambiguous interpretation of the results.

2. The gradientless reactor gives best opportunity for precise and reliable measurement of catalytic activity of industrial catalysts.

3. Contemporary multichannel reactors for heterogeneous catalytic reactions can be used successfully for preliminary screening of catalysts.

4. Detailed testing of the activity of the catalyst is expensive and time consuming and should be done on the catalysts that have already passed other chemical, physical, mechanical and physico-chemical tests.

5. Catalytic activity tests can provide reliable and precise data only if the laboratory catalytic reactors are properly selected according to the specific features of the process and catalysts under study.

6. Heterogeneous catalytic reactions are always accompanied by processes of heat and mass transfer. The characteristics of the internal and external diffusion regimes on single catalyst grain shall be presented shortly.

7. It is essential, that the analytical methods and equipment used for analysing the compositions of reaction mixtures at the reactor’s inlet and outlet are precise, fast, and reliable. We will not discuss further this problem.

8. Interpretation of the results from catalytic activity tests should be done always taking into account the results obtained from the application of other characterisation techniques - chemical, physical, morphological and mechanical. Very important in this sense is the opportunity to combine catalytic activity measurements with application “in situ” of some physical methods by which the additional information about the catalyst changes during the catalytic runs can be obtained.

9. In order to obtain reliable and reproducible results from the measurements of the catalytic properties of industrial catalysts it is very important to use a large amount of catalyst probe (taken as mean probe according to the standardised sampling procedure) a source of catalyst charges for laboratory reactors. Industrial catalysts grain - pellets,

extrusions, granules, and microspheres for fluidised bed reactors are not ideally homogeneous. For example, samples taken from the top and the bottom of the tank in which they are transported and stored are usually not identical. The same is valid for samples taken from different tanks or different charges.

10. The methods for testing of catalytic activity are individual for every type of catalyst. Every catalyst producer has own catalyst composition. For this reason producers and user have developed their own standard testing procedures which differ from company to company.

11. As stated above, industrial catalyst production is of strategic importance for any developed country and without doubt it belongs to the category of the so-called 'high tech' industries. It should be emphasised that without intensive research and development activities it is impossible to reach and maintain a high level of catalyst production. In view of the above considerations, industry should play the leading role, which is especially important. As one of the chief employers and main consumer of research products, it is expected that industry will be the main initiator that will understand and define existing and future problems and find their solution. It has to be the provider of funding for R&D teams.

The progress of chemical industry depends on its attitude toward chemical science and interest in research work, while the good shape of science is determined by the fact how far it turns its face to the demand and prospects for developments in industry.

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