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Review

Design of complexity of industrial catalytic systems — impulse oscillation model studies

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Abstract

This review points out the role of a system view in design of a complexity of real new catalytic systems and presents an overview of fundamental theoretical and experimental information necessary to describe the proposed common approach to homogeneous, heterogeneous and enzyme catalysis. The problem of design of the complexity of efficient catalytic molecular devices is divided into three aspects: *general model of the complexity*, from which general rules of construction and behaviour of the devices result — in particular — energy and time requirements for catalytic reaction to occur at the molecular level; *application of the general model* to show practical aspects (selectivity, minimum value of activation energy and live-time of the catalytic system) of the energy requirements and to present good agreement between experimental evidences and prediction of the model in analysis of multienzyme systems; *application of the impulse oscillation model (IOM)* for calculation of the time requirements. Examples of application of the IOM in homogeneous (the reaction of CO_2 with amines and the synthesis of organic carbonate) and heterogeneous (the isomerization of the butene-1 and the decomposition of HCOOH) catalysis illustrate the possibilities of the IOM to be used as a practical tool for design of improved or new catalysts. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Four basic needs of society, namely, health care, food supply, energy and materials can be fulfilled, in a way that provides a path to environmentally sustainable development, with improved or new tailored-made catalysts [1]. Therefore, efficient methods of design of new industrial catalysts maximising the yield of a desired product, at commercially acceptable conditions, with no or minimal by-products are necessary. Such design seems to be a long-term goal. In industrial practice, serendipity [2] and high-risk exploratory research [1] are still important factors in innovation. From the recent list of gaps, needs and challenges in industrial catalysis [3] it follows that a common theoretical and practical approach to homogeneous, heterogeneous and enzyme catalysis and a conversion of molecular level description of catalysis into a form useable to an engineer–designer of

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catalytic reactions system at real scale should be the most important long-term targets of oriented basic research in catalysis.

Industrial catalysts (still mostly heterogeneous) are usually [4] very complex dynamic systems. Therefore, in modern industrial catalysis macroscopic level description of the catalysts has been preferred, i.e., experimental studies of known catalysts and design of improving ones by analogy. This approach has been used with success in practice. It is expected that combinatorial chemistry approach [5] will have direct or indirect value in improvement of efficiency of the heterogeneous catalysis research.

However, the macroscopic level description possesses a few inherent disadvantages, which cause difficulties of the design of really new catalysts. First of all, it is difficult to single out the catalytic function from transport and sorption phenomena, which usually are important factors determining the overall catalyst performance under conditions of industrial process. In order to search for a new catalyst it is more convenient to look separately at the catalysis phenomenon, design active and selective reactive sites, and then try to find optimum macroscopic conditions, which can be quite different than these for a known catalyst. Indeed, there are many examples (e.g., the methanol synthesis, the cracking zeolite catalyst, etc.) in industry, when introduction of a new type of catalysts caused radically changes of the process conditions.

However, the most important disadvantage is a model of statistic representation of a population of active sites of a considered catalyst, which has been used in the approach. In the model, the active site has catalytic properties averaged over the whole population of assumed number of active sites of a known considered catalyst. Such model has limited prediction of new catalysts, because, as it was pointed out [6], both selectivity and activity are functions of the chemical makeup of a particular catalytic site and the heterogeneous catalyst has the multisite nature. In general, the averaged representation

of the sites property can be justified only in a particular case, when a heterogeneous catalyst has the normal distribution of the properties of active sites in their population and the desired property is dominated one in the population. In most cases, this cannot be true. Therefore, in order to predict, for instance, the activity of a catalyst from first principles, one must know the distribution of the site activity among available sites.

An opposite approach — starting from microscopic level of description, i.e., from a pure theoretical model of ''naked'' active site or from experimental model of a super cleaned surface studied by a huge number of highly sophisticated techniques — has developed our basic knowledge of catalysis, but did not be helpful for designer of industrial catalytic reactions system at real scale and conditions. Therefore, a more effective computer-aided design of catalysts is one of the most important challenges in present theoretical and industrial catalysis. In particular, in theoretical catalysis the most important purpose of oriented basic research is to predict the performance of a catalyst based on the knowledge of the reactive site [7].

During the last decade rapid progress in computational chemistry and development of quantum chemistry and other theoretical models in catalysis has been made. The modern state of art of the theoretical catalysis has made readily available detailed understanding of the governing structural and electronic features of adsorbate–surface interactions as well as good predictions of properties (structure and energetics) of many simple molecular catalytic reaction systems. Quantum-chemical methods, starting from semiempirical to first-principles techniques as well as famous empirical methods like the bond order conservation method and, last not least, the well-known transition state reaction rate theory, using modern computers have became useful tools in description of elementary steps in catalytic reactions of simple molecules. The cluster approach and the density functional theory seem to be the most promising directions in

the path toward the long-term goal of catalyst design. There are some excellent reviews and books [8–12] summing up the tremendous volume published in this area.

Despite of the great possibilities of the modern quantum chemistry, it is still necessary to make many approximations in the models of real catalytic molecular systems in order to obtain results in an acceptable time of computation. This fact proceeds from technical rather than theoretical problems. Therefore, there are few limits of the quantum mechanical studies of catalytic systems. The most important limit is size of the system: only medium size systems can be studied, while in practice the most important are larger real systems. Moreover, understanding of the structural and electronic features determining interactions important for catalysis and good predictions of properties (geometrical structure and energetics) are available for a well-defined closed molecular catalytic reaction system, i.e., for an assumed catalytic active site (or another simplified model of catalyst) and a considered molecule of reactant. Therefore, it is much easier to explain why a known catalyst is catalyst, than to predict a new catalyst for a desired reaction.

In industrial catalysis the main practical goal of the development of design of catalysts seems to be searching for tools, which can be used by the designer of catalytic reactions system at real scale and conditions. In this case, the importance of a system view is recently pointed out [4]: The performance of a given catalytic system represents the combination of a set of properties. A given property is dependent on the geometrical structure of the total system, and of its components, both at the atomic level (the ground state electronic structure being defined by the geometrical structure) and at longer length scales such as the mesoscopic. Structure is controlled by the conditions of synthesis and processing.

This systems view highlights the desirability, not only of detailing each of these separate facets of the system, but, particularly, of understanding the interfacet links, how the synthesis and processing conditions affect the various structural attributes, how the individual properties are controlled by the structural details, how the combination of a defined set of properties governs the overall catalyst performance.

The aim of this article, addressed to both theoreticians and industrial experimentalists, is to give an overview of proposed by the author one of possible system views to modeling of catalytic system.

The first part of this paper is based upon studies have been carried out by the author and upon selected information from the literature. It will be shown that general considerations, characteristic for any system view approach, lead to a simply model of any elementary catalytic system (named ECS). General rules of construction and behaviour of the ECS, in particular, energy and time requirements for catalytic reaction to occur at the molecular level, will be presented. Practical aspects (selectivity, minimum value of activation energy, live-time of the catalytic system) of the energy requirements will be discussed. The good agreement between experimental evidences and predictions of the model applied to biophysics for analysis of the multienzyme systems will be shown.

In the next paragraph, a practical tool for calculation of the time requirements will be described — starting from the discussion of molecular recognition, in particular of a role of chemical information carried out by molecule, up to description of a proposed Impulse Oscillation Model (IOM). The main idea of the IOM is to use frequencies of vibrational modes as primary time parameters (vibrational periods) — treating both a reactant molecule and an active site as sets of vibrators. As it will be shown, application of this idea results in drastically simplification of the model calculation. It made possible to use the IOM for more realistic complex catalytic systems in order to find optimum ranges of the frequencies of the sets of vibrators for a desired catalytic reaction to occur. The ranges can be treated as receipts for design efficient new catalysts.

In the second part of this paper, examples of practical applications of the IOM, which have been carried out by the ICRI team in cooperation with European teams of theoreticians and experimentalists (the COST Actions), should illustrate the possibility of the proposed model to be used as a practical tool for catalyst design.

2. System view to catalysis phenomenon

In order to search for new catalysts for a desired reaction, a system of known reactants and unknown potential catalysts should be studied. It is well known that the purpose of catalyst performance is to activate and to incite molecules to react along a desired reaction path. Catalyst and activated reactant molecule, due to interactions between them, are immersed in a specific potential field, which causes changes of properties of both of them. As the consequence of these changes, the desired catalytic reaction occurs. A question is what potential field, or what changes of the molecule properties are needed for a desired catalytic reaction to occur? The answer to the last question seems to be easier than to the former one. Indeed, one can use a known reactant molecule as the indicator of a desired potential field in a catalytic system and from the predicted changes of the molecule calculate the field and next find the catalyst creating such field. The two last steps calculations seem to be resolvable with advanced quantum chemistry methods. To resolve the first step, tools for prediction of the changes are needed. Simple, but reasonable, general description of catalytic behaviour of the reacting system is necessary.

The description of singled-out catalysis function must combine together the following three aspects of catalysis:

- spatial (a reactant molecule should be syn-fixed with a catalytic center);
- energetistic (energy fluxes and energy effects)

- temporal (a sequence of elementary events constituting the catalytic act)

The two first aspects have been studied at macroscopic and microscopic levels from many years, while the last one is described usually at macroscopic level basing on kinetics studies which do not incorporate [13] the basic surface chemistry involved in catalytic reaction. The microkinetic approach [13] seems to be promising in design of catalyst by analogy with known ones.

The key problem in the common description of the three aspects of catalysis is a set of connections between spatial, energetistic and dynamic properties of elements constituting any molecular catalytic system. Some modern concepts in the theoretical catalysis have pointed out such connections. Haber [14] stated that heterogeneous catalytic act occurs within a two dimensional phase which properties are different from those of solid and gas phases. The connection between energetistic properties of catalyst (the heat bath) and those of reactant molecules is visible from Larsson model [15,16] of selective energy transfer, which in many reactions is able to explain the isokinetic relationship and predicts [17] some connections between geometric properties of catalyst and the observed values of activation energy. The macroscopic dynamic changes of the catalyst surface [18] and those on the surface [19], as well as the found [20] role of short lifetime intermediate species on the surface in determining reaction pathways clearly show importance of temporal aspect of catalysis at molecular level. In a description of the time-dependence of catalytic act it is necessary to avoid misunderstanding between famous descriptions of the dissipate patterns at macroscopic level based on diffusion–kinetics coupling (time scale order from seconds to minutes) and molecular level picture of singled-out catalysis function (much more less than second).

The main reason of problems in development of simply tools useful in design of industrial

catalysts seems to be a complexity of reacting catalytic systems. One may assume that just the complexity is the primary reason of catalysis. In such approach, one has to address the question: what type of complexity should be design in a molecular system in order to obtain the catalytic system, instead of the commonly used one: why a known catalyst is the catalyst? The simplest way to answer the first question is to look for a general model of the complexity using a system view.

In spirit of a concept of the molecular devices, developed by Lehn [21] in supramolecular chemistry, it can be assumed that any catalytic molecular device should be structurally organized and functionally integrated molecular system. While any enzyme or any homogeneous catalyst could be directly treated as such device, any heterogeneous catalyst can be considered as a set of the devices. To design a catalyst basing on this assumption one has to known general rules of construction of catalytic device, the rules and methods for coupling the devices to build a larger, organized system (e.g., multienzyme or heterogeneous catalytic systems) and has to take account of the interaction of the single or the organized systems with a stochastic environment containing reactants.

The general model of catalytic molecular device should based on general principles in catalysis, which result from a set of common features of enzyme, homogeneous and heterogeneous catalysis, rather than from features, which make them discernible. Using such model for design of a particular catalyst for a desired reaction one has to translate the general principles into necessary particular properties of active site depending on particular properties of reactant and product in the reaction.

A description of catalytic act inside the molecular catalytic device should take into account all, but only events which cause catalysis. Therefore, the transport processes of reactant to and of product from the device, as well as the sorption processes should not be included in the description. Indeed, the transport depends on

properties of an environment of the device while not any sorbent is a catalyst. Inside the device molecular energy, space and time scales parameters have to be used. The first step is to make the common description of catalytic chemistry of making and breaking bonds in molecular device.

2.1. General model of catalytic molecular device

The proposed [22] general model (Fig. 1) of catalytic molecular device is the simplest molecular catalytic system where a single catalytic elementary act can occur. It means that it contains all, but only those elements and interactions, which are necessary for the act to occur. The model is named ECS.

The ECS model describes the behaviour of a single catalytic center with its microenvironment containing a stoichiometric amount of reactants before the catalytic act and of products — after the act. A local source of energy g and a local receiver of energy k had to be added in the microenvironment in order to make it possible to consider a single catalytic act inside the device isolated from its environment. Molecular energy, space and time scale parameters are used [22] for the description of the act.

As it was expected in the light of Lehn's concept [21], in the functional integration of catalytic molecular devices chemical information storage at molecular level and adjustment of the energy quanta play the important role. Catalysis results from the complexity of the device and not from a sum of properties of the elements constituting the device. The complexity of the device is necessary in order to organised well-defined conditions for: (a) directed fluxes of appropriate energy quanta from the source of energy g to the center c (the (g,c) interaction) and to the substrate s (the (g,s) interaction) — the two events of activation process, as well as from the center c (the (k,c) interaction) and from the product p (the (g,c) interaction) to the receiver of energy k (receipt
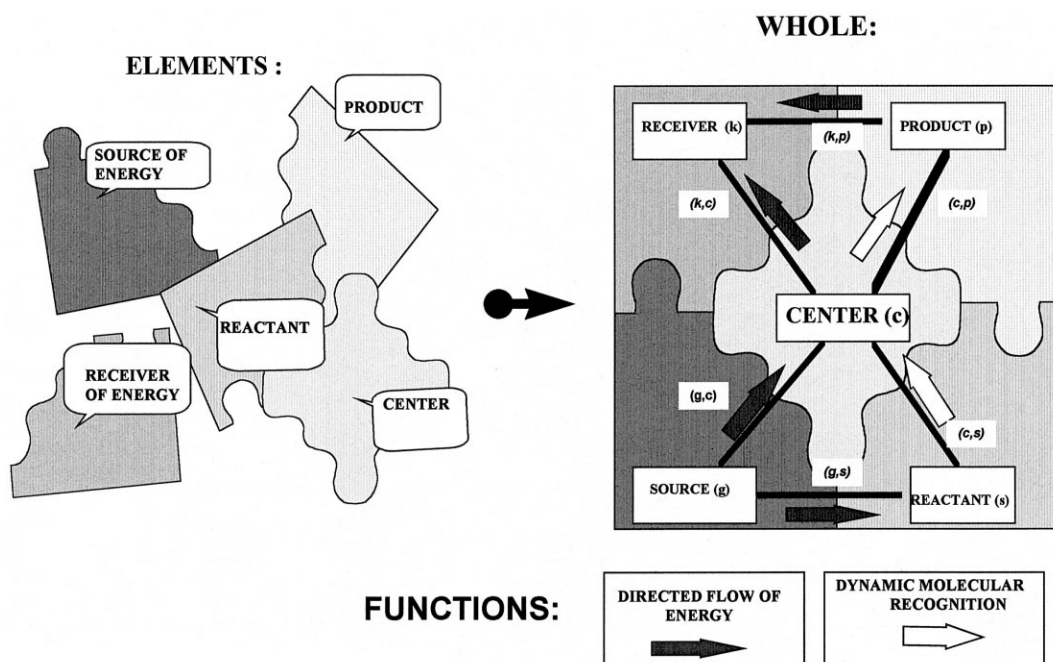
ELEMENTS :

WHOLE:

FUNCTIONS:

Fig. 1. The general model of catalytic molecular device: the Elementary Catalytic System (ECS). The five elements, namely catalytic **c**enter (c), reactant (**s**ubstrate = s) and **p**roduct (p) molecules, local source of energy (''**g**enerator'' of energy = g) and local receiver of energy (''**k**ick out'' of energy quanta = k) are the building units. The six bi-elements interactions (elementary events constitute elementary catalytic act), namely (g,s), (g,c), (c,s), (c,p), (k,p), (k,c), create with the elements a functional whole (the ECS). For more information see the text.

of activation energy and energy effect of the reaction in order to make impossible the reverse reaction); (b) dynamic process of molecular recognition (the (c,s) and (c,p) interactions) (at the supramolecular level reading out of information carried by reactant and the center and depend on molecular size, shape, architecture and time [21]).

The following most important general rules of molecular devices construction resulted from the proposed system view can be formulated [22]:

1. Any catalytic molecular devices should contain the following five components: catalytic center, reactant, product, source of energy and receiver of energy.
2. Complexity of the device can be described by at least six interactions between the components.

3. A chemical individuum can serve as an active site if — and only if — it can exist in minimum four different states of its allowed internal energy levels. (The same number of the necessary states is postulated for enzymes by Ricard [23]).
4. To create within the device the directed fluxes of appropriate energy quanta it is necessary to use as the source and as the receiver components, which can exist in minimum three different states of their allowed internal energy levels.
5. The choice of appropriate source of energy and appropriate receiver of energy for a given center and for given pair of reactant and product molecules depends on fitting of differences between the energy levels of the components.
6. For the fitted source of energy, center and receiver of energy, one and only one pair of

reactant and product molecules can be found. The organized directed fluxes of energy quanta determine the selectivity of catalytic reaction.

7. For a desired pair of reactant and product molecules, there are many possible devices but number of the possibilities is finite number. A desired reaction can be realised using different catalysts.

2.2. Role of energy in the functional integration of the device

It is well known that any chemical reaction can be characterised with two energy parameters, i.e., with energy effect of a reaction (ΔG), which is independent on pathway of the reaction, and with activation energy (ΔE_a), which depends on the pathway. In particular, different catalysts are usually described in macroscopic and microscopic levels with characteristic different values of the activation energy. Therefore, any efficient catalytic molecular device should posses ability to control its characteristic value of activation energy of catalysed reaction. Moreover, the device should be also able to return the center from its energy state at the end of catalytic act to the state before the act. The latter requirement results from the very definition of catalysis. If it is not fulfilled, the device just after transformation of reactant into product will be ready to transform product into reactant (catalyst does not shift equilibrium constant of reaction), just after that will be ready to transform reactant into product etc. There are the reasons while, in order to design an efficient molecular catalytic device transforming reactant molecule into a desired product molecule, it is necessary to organized flows of appropriate energy quanta in the device. In the ECS model general rules of the organisation are defined (see the rules 4–6 above). In any particular case study, the choice of the appropriate source and the receiver is well-defined with allowed energy state levels (including the ground states) of reactant, catalytic center and product, because the differences between the allowed levels have to fit to the appropriate differences between the levels of the source and the levels of the receiver of energy quanta, respectively. It means that in the efficient catalytic molecular device, these energy levels differences are not independent and the energy requirements are important in the functional integration of catalytic molecular devices. Indeed, the choice of local source of energy means, in fact, the choice of value of activation energy (determining reaction path), while the choice of local receiver of energy depends on the sum of the activation energy and energy effect of the considered reaction. Therefore, the choices determine one and only one value of activation energy characteristic for the device and one, and only one, possible reaction. These general statements, resulted from analysis of ECS model [22,24–26], show the role of organisation of directed energy quanta flows in the functional integration of catalytic molecular devices.

The question about mechanisms of reactant activation in heterogeneous catalytic system, how and from where the necessary energy is delivered, was systematically studied by Larsson [15–17] and was considered by Bond [27]. Classical assumption (for instance, in the absolute reaction rate theory), about equilibrium between the reacting molecule and the molecules in population, can be in many cases of catalytic systems insufficient for description of catalytic reaction, as it was shown by Krylov and Szub [28] in their book. They also pointed out the fact that energy of chemisorption of reactant on catalyst surface is much larger then characteristic energy of phonons of typical heterogeneous catalysts. Therefore, the process of dissipation of the chemisorption energy must be multi-phonon one, and, as a consequence, the dissipation is not immediately. This conclusion is valid also for the dissipation with excitons. On the metal surfaces, the lifetime of excited electronic state is a view hundred femtoseconds, while the

lifetime of excited oscillation state on metal oxides surface is 200–260 ps.

According to the ECS model, the activation energy is the sum of activation energy of the centre ($E_{c1} - E_{c0}$) and of the activation energy of reactant ($E_{s1} - E_{s0}$):

$$E_a = (E_{c1} - E_{c0}) + (E_{s1} - E_{s0}), \tag{1}$$

obtained from the energy source g. The elementary catalytic act can run, if and only if, there are allowed states E_{s2} and E_{c2} such that:

$$(E_{c1} - E_{c0}) + (E_{s1} - E_{s0})$$
$$= (E_{c1} - E_{c2}) + (E_{s2} - E_{s1}). \tag{2a}$$

or

$$(E_{c1} - E_{c0}) + (E_{s1} - E_{s0})$$
$$= (E_{c2} - E_{c1}) + (E_{s1} - E_{s2}). \tag{2b}$$

In other words, due to interaction between the activated center and reactant, the energy transfer causes activation of reactant molecule in such an extent that the reaction occurs. There are two possible directions of the energy flow. The first one (Eq. 2a) from the center to reactant, the second (Eq. 2b) — from the reactant to the center. In the latter case, activation energy is always higher in comparison to the first one for the same desired catalytic reaction system. Notice that in industrial practice the case (Eq. 2b) has been used, because it is easier to make thermal activation of the set of reactant molecules than to organised well-defined direct flow of energy quanta in heterogeneous catalyst. In such set of molecules the Maxwell–Boltzman distribution of energy exists. According to the ECS, only small fractions of the excited molecules can fit to the well-defined centre. One can say that from the point of efficiency of use of energy, it is better to strike a match (activation of the catalytic center) and use it to strike a wick of candle (part of reacting molecule) rather than to put all set of candles and matches into a hot furnace.

Starting from the simple relations (Eqs. 1 and 2a) and using the harmonic model one can obtain the equation:

$$E_a = h\omega_s [N_{s1} + (N_{s2} - N_{s1}) + N_{c2} h\omega_c / h\omega_s]. \tag{3}$$

where $h\omega_s$ and $h\omega_c$ — differences between energy levels in reactant and in the center, respectively. From the Eq. (3) it is easy to find the minimum value of the activation energy $E_{a(harm)} = 2h\omega_s$, i.e., one equals to two difference between energy levels in reactant (indeed, for: $N_{s1} = 1$; $N_{s2} = 2$; $N_{c2} = 1$ and for $h\omega_c / h\omega_s \ll 1$ the value in bracket runs to 2). Anharmonicity decreases value of activation energy :

$$E_{a(harm)} - E_{a(anharm)}$$
$$= h\omega_s [N_{s1}(N_{s1} + 1) x_s$$
$$+ h\omega_c N_{c1}(N_{c1} + 1) x_c / h\omega_s], \tag{4}$$

where x_s and x_c are the anharmonicity coefficients. For instance, for these coefficients equal to 0.05, $h\omega_c / h\omega_s = 0.01$, $N_{s1} = 1$ and $N_{c1} = 62$ the difference (Eq. 4) is equal $2h\omega_s$, i.e., $E_a = 0$. Thus, the minimal true theoretical activation energy in the ECS model varies [29] from $2h\omega_s$ to 0, depends on anharmonicity in the reacting system and the ratio of energy levels in substrate and centre.

There is the well-defined [27] relation between the true activation energy E_a and the experimental one: $E_e = E_a - \Delta H_s$, where ΔH_s is enthalpy of adsorption of substrate. Unfortunately, it is difficult to make a comparison between the experimental and the estimated above theoretical minimal activation energies because of the lack of appropriate experimental data. Most of experimental data, particularly in heterogeneous catalysis, give the values averaged over whole population of active sites, which are heterogeneous at the microscopic level. One can expect that the value of activation energy of hydrogen peroxide decomposition reaction on catalase should be nearest the minimal theoretical one, because the catalase is

one of the most active known catalyst. The experimental activation energy found in literature is 1.3–2.0 kcal/mol. Assuming that the determining step of the reaction is the O−O breaking step, the true lowest theoretical activation energy is equal 5.0 kcal/mol and ΔH_s should be 3.7–3.0 kcal/mol. If the determining step is the O−H breaking, then for the case of activation of the O−H symmetric stretching mode ΔH_s should be 15–14 kcal/mol, while for the case of activation of the O−H asymmetric stretching mode ΔH_s should be 18–17 kcal/mol [29]. Experimental measures of the ΔH_s can show what is the mechanism of the decomposition reaction.

According to the ECS model, more profitable (the lower activation energy) is to organise the directed flow of appropriate energy quanta from the catalytic centre to reactant molecule. The experimental evidence, e.g., [30,31] that natural enzyme systems posses mechanisms for vectorial flow of energy seem to confirm this concept. It is well known that majority of energy flows inside solids are discrete (quasiparticles of elementary excitation). It is also well known that, e.g., phonons are trapped by crystals defects. There are many examples of heterogeneous catalysts with crystal defects serving as very active catalytic sites. These facts may be related to the necessity of directed flow of energy during the elementary catalytic act. Systematic studies of Somorjai [32] have shown how to use it in practical heterogeneous catalysis, controlling types of defects. From the point of view of the ECS model, the most efficient way to decrease the activation energy is to excite any active site instead of thermal activation of a desired set of reactant molecules. The decreasing of activation energy should be also observed in heterogeneous catalysis, if one will excite the surface of catalyst (activation of population of active sites) instead of the activation of substrates. Indeed, such decreasing effect was observed by Inoue et al. [33] who used surface acoustic wave (SAW) for activation of surface of catalysts. One can expect higher decreasing

of activation energy if it will be possible to use solutions of SAW instead of the collective wave. Very promising in this field can be also electrocatalysis and supramolecular chemistry. The most important for future rational design of the organisation of directed flows of energy quanta is the knowledge how many and what type of the quanta are necessary in a desired catalytic system. Systematic studies in this direction has been carried out by Larsson [16,17] using the selective energy transfer (SET) model.

According to the ECS model, the organised directed flows of appropriate energy quanta from the center and from the desired product to the local receiver of energy k are necessary. This process determines, at molecular level, possibility to stop the reverse catalytic reaction, i.e., to increase a turnover number of catalytic molecular devices. On the other hand, different organisation of the process can dramatically change selectivity and lifetime of the device and consequently, in particular, averaged selectivity and lifetime of designed heterogeneous catalyst. In experimental catalysis there are a lot of example of fresh prepared catalysts possessing very good activity and selectivity in short-term laboratory tests but losing rapidly these properties in long-term tests. There is a huge number of papers explaining reasons of deactivation of particular catalysts, but in the light of the system view presented in this paper, the main reason seems to be an improper organisation of the flow of energy excess from the product and from the catalytic centre at molecular level. Indeed, just after transformation of a reactant into a product of a desired catalytic reaction, the product molecule can: (i) leave the active site; (ii) block the active site after rapid losing of excess energy; (iii) begin the opposite reaction; (iv) begin a consecutive reaction. The case (i) is possible if — and only if — the product molecule, at the moment of leaving the site, posses excess of energy greater than the heat of desorption because the molecule needs a kinetic energy for migration on the catalyst surface or for leaving the surface. Notice that just after the reaction a
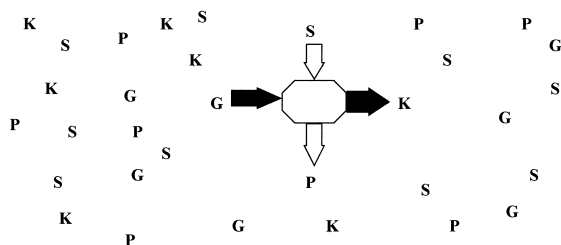
Fig. 2. The Elementary Catalytic System (ECS) interaction with its stochastic environment. The ECS is treated as a transformer of the chemical (s) and the energy (g) input signals into the respective output signals p and k. The maximum classical probability for an elementary catalytic act (ECA) to be realised by the ECS–MPr $(ECA)_1^f = 2.5 \times 10^{-9}$ (see the text).

multiphonon process of energy dissipation in solid has started. If the time of dissipation is shorter than the relaxation time of molecule to be ready to desorb the case (ii) occurs. If the time of dissipation is much longer than the time of beginning the opposite reaction the case (iii) occurs. If the time of full dissipation of energy is longer than the time of a consecutive reaction the case (iv) occurs. More quantitative analysis of the time is possible using the impulse oscillation model (IOM) described in this paper below.

In general, it is well known [28] that the rate of dissipation depends on properties of solid. A piece of solid, used as a catalyst, has a finite volume and has to collect consecutive energy quanta produced in consecutive catalytic acts. Therefore, a macroscopic correlation between the specific heat of a solid, used as a heterogeneous catalyst, and the catalyst properties in the same macroscopic conditions should exist. Unfortunately, there is lack of such experimental data in literature.

In homogeneous catalysis molecules of solvent should play the role of receivers of energy k. One can expect that the well-known strong solvent effect in this catalysis may be partially explained with this important role. In enzyme catalysis, the cell and organelles membranes can be considered as the receivers of energy, but the most important seems to be the role of energy coupling in multienzyme systems. This will be discussed below.

2.3. Interaction of ECS with its environment

Single ECS model of catalytic molecular device can describe requirements for occurring of a single elementary catalytic act. To make many acts run in succession in the device, it is necessary to carry away the resulting energy portion and the resulting product from the device to its environment and to deliver another portion of energy and another reactant molecule to the device.

While an elementary catalytic act occurs, the catalytic center c is following a closed trajectory in its state space (the regeneration of c — the (k,c) interaction), thus the ECS model may be simplified and considered a transformer of the chemical (**s**) and the energy (g) input signals into the respective output signals p and k. In the light of this model an optimum organisation of the ECS environment will consist of a sequence of the catalytic act events synchronised and syn-fixed in delivery or reception of suitable objects in appropriate states at correct ECS input/output (Fig. 2). One way to model the organisation is to use another ECS as the source or the receiver of the signals required in a given ECS.

The simplest organised catalytic system is the system of two coupled ECSs. This system will act [34–37] provided the defined appropriate time and energy relationships are satisfied. The energy (Fig. 3) and chemical (Fig. 4) couples
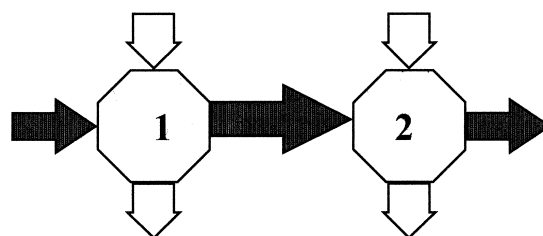

Fig. 3. The simplest organised catalytic system of two energy coupled ECSs. The receiver of energy in the first ECS is simultaneously the source of energy in the second ECS. The coupling of two ECSs caused the increase of effectiveness of action of each ECS at least by a factor of several hundred (see the text).
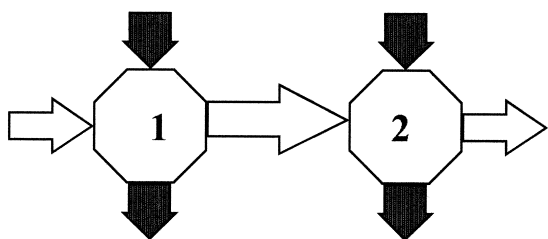
Fig. 4. The simplest organised catalytic system of two chemically coupled ECSs. The product from the first ECS is simultaneously the substrate in the second ECS. The coupling of two ECSs caused the increase of effectiveness of action of each ECS at least by a factor of several hundred (see the text).

are examples of deterministic models of cooperation of ECS with its environment.

The models of two coupled ECSs may be treated as the fundamental structure units of organised multicatalytic system (MCS) containing more than two ECS. From the point of view of the couple we can distinguish [34–37] energy coupled, chemically coupled and mixed MCSs, while taking into account structure — chain, ring and dendrites MCSs (Fig. 5). It was proven [35,36] that the ring structure of energy-coupled ECSs is impossible. For the chain and ring structures the number of ECS contained in a MCS was shown [34,35] to be a finite number.

This means that in a hypothetical infinite set of ECSs, it would be possible to construct an infinite number of MCSs containing finite numbers of ECSs, but it would be impossible to build one MCS containing an infinite number of ECSs. This general conclusion is intuitively consistent with the modern theory of evolution [34].

To follow the effect of a stochastic environment on the performance of an ECS (or a MCS), models of organised catalytic systems immersed in their stochastic environment were studied [35–37]. The events occurring inside the ECS (or MCS) were assumed to proceed in a deterministic manner, i.e., with probabilities equal to unity. From the assumption the environment was non-ordered (stochastic behaviour), but well defined as concerns the numbers of objects, object states and of the inputs/outputs with which it interacted with deterministic catalytic system. In the build models a notation of maximum classical probability for an elementary catalytic act (ECA) to be realised by an ECS—MPr(ECA) was used. Assumptions made in the models caused that the estimated values of the MPr(ECA) were rather too high, but not too low.
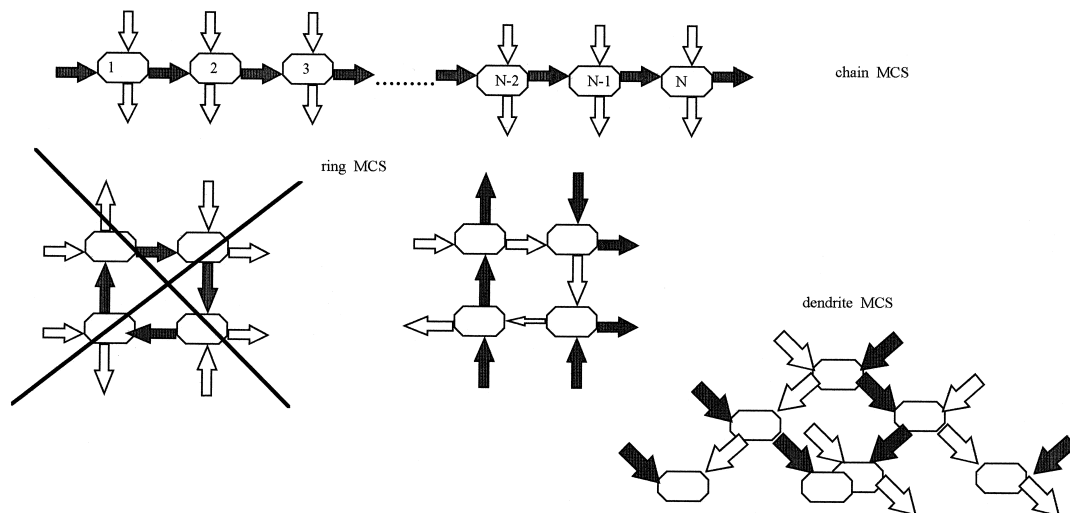

Fig. 5. Example of possible structures of the Multi Catalytic Systems (MCS). It was proved [35,36] that the ring structure of energy-coupled ECSs is impossible.

For a single ECS immersed in the stochastic environment containing four objects (s, p, g, k) the calculated [35] $MPr(ECA)_1^f = 2.5 \times 10^{-9}$ (where the superscript ''f'' (free) means that the ECS is noncoupled and the subscript ''1'' is the number of ECSs in the model). In a more complicated model consisting of n noncoupled ECSs immersed in the stochastic environment containing $4n$ objects the MPr $(ECA)_n^f = 2.5 \times 10^{-9} \times n^{-8}$. For instance, for $n = 5$ the MPr $(ECA)_n^f = 6 \times 10^{-15}$ and for $n = 10$ the MPr $(ECA)_n^f = 2.5 \times 10^{-17}$. As the number of various ECSs immersed in the stochastic environment is increased, the individual free ECS becomes less and less likely to act. The coupling of two ECSs causes the increase of effectiveness of action of each ECS at least by a factor of several hundred ($MPr(ECA)_2^f \cong 10^{-11}$ while MPr $(ECA)_2^c \cong 10^{-8}$, where the superscript ''c'' means that the ECSs are coupled [35]). The effect ($\approx 10^2$) due to chemical coupling is by at least one order of magnitude higher than that established in the kinetic studies on immobilisation of bienzyme systems like fumarase–malate dehydrogenase and malate dehydrogenase–citrate synthase on porous glass beads [38] and others [39]. The rise in effectiveness was 10-fold in the former and 40–50-fold in the latter studies. The discrepancy may be both due to the nonfulfillment of the general assumptions adopted in the evaluation of the MPr(ECA) estimates and due to technical difficulties encountered in producing correct coupling in vitro [36].

In more complex MCSs, absolute values of the probability decrease with increasing number n of ECSs constituting the MCS. For instance, a general formula [36] for the probability of action of each nonterminal ECS in the chain, energy-coupled MCS immersed in its stochastic environment containing $4n$ objects is MPr $(ECA)_n^c = 3 \times 10^{-4} \times [n(2n + 2)]^{-2}$. The decrease is smaller in comparison with the decrease of the $MPr(ECA)_n^f = 2.5 \times 10^{-9} \times n^{-8}$, i.e., in the model of n free ECSs immersed in the environment containing also $4n$ objects (for

$n = 5;10;100$, the probability for noncoupled ECSs is 10^{-15}; 10^{-17}; 10^{-25}, and for coupled ECSs 10^{-6}; 10^{-7}; 10^{-8}, respectively). On the other hand, it seems to be unprofitable to create an multicatalytic system in which each ECS constituting the MCS will act with efficiency lower than 2.5×10^{-9}, i.e., those accessible in the single free ECS. Using this criterion, it was shown [36] that formation of ring and chain MCSs is profitable with ECSs not exceeding 20 in number. The estimated number is in full agreement with results of experimental enzymology.

In real catalytic systems an environment contains not only the necessary objects, which participate in the events, constitute catalytic act, but also other objects not necessary for the act to occur. The latter ones may consist, e.g., of molecule of solvent in a liquid phase system. Models [37,40], which take into account the presence of such redundant objects use a coefficient α defined as the ratio of the number of the objects necessary for the act and the number of the redundant objects. The MPr(ECA) is a function of the coefficient α and of the number n of ECSs constituting the MCS. With increasing of the coefficient α the probability increases but for $\alpha > 1$ even very large changes of α cause only a little change of the probability. For very small α it is profitable to create very large MCSs, but the values of the MPr(ECA) are very low (e.g., the probability is equal to 10^{-29} for $\alpha = 10^{-9}$ and $n = 108$). The optimum — from the point of view of the probability — percent concentration of proteins was estimated [40] using experimental data of averaged molecular weight of the proteins in the mitochondria [41]. The calculated concentration fits very well with the experimental one [41].

3. Impulse oscillation model

According to the ECS model, chemical information storage at molecular level plays the important role in the functional integration of cat-

alytic molecular devices. Organisation of optimum conditions for the dynamic process of molecular recognition in an efficient device is necessary for the catalytic act to occur. In order to transform these general conclusions to practical tool for design of the devices, the Impulse Oscillation Model (IOM) was proposed [34] and developed [22,24–26]. The model has been developed basing on the concept of molecular recognition and a definition of chemical information.

3.1. Dynamic molecular recognition

The molecular recognition has been defined [21] as ''a process involving both binding and selection of substrate by a given receptor molecule, as well as possible a specific function'', as a consequence of numerous noncovalent binding interactions depending on the molecular size, shape and architecture. Molecular recognition is thus a question of information storage and read out at the supramolecular level. Notice that in the light of Stuart considerations [42,43], information notion should be use with great caution. He clearly shown that in many works — in particular, using the bio-information notion — it is overused. To avoid this, one has to remember that from Lehn's definition [21] it is clear that molecule is not the chemical information, it is a carrier of the information available for another molecule to read it out.

Based on the classical theory of information [44] a formal definition of chemical information was proposed [45]. This definition made possible to introduce a model of molecule, in which it is postulated that the trajectory of states of molecule as a whole in its states space is closed curve with no intersect points. The time of run along the trajectory is characteristic for a given molecule at its one of allowed energy states. In particular, for the ground state any molecule is a carrier of the chemical information (CI), while for any other allowed states — of the excited chemical information (ECI).

How a molecule can recognise characteristic size, shape and architecture of another molecule? The only ''sense'' which posses molecule is the sense of feeling of a potential field of the another molecule. Mezey [46], on the basis of topology, has described size and shape of molecule from the point of view of the concept of molecular similarity, using an electronic charge density parameter. The 3-D shapes of molecular electronic charge densities can be represented by isodensity contour surfaces. For a large value of the parameter, the surface is composed of several disconnected, essentially spherical surfaces, each surrounding one nucleus. For very small contour value, the surface contains no information on the shape of the molecule (essentially spherical balloon surrounding the nuclei is created). However, it was [46] pointed out that, molecules are nonrigid, topological objects and the description of their shape and similarities requires models that take into account their dynamic nature. The entire family of nuclear geometries, representing the dynamic shape was proposed by Mezey.

The definition of chemical information [45] simplified the description of the dynamic molecular recognition. The chemical information is in fact a time–space description of momentary electron density distribution in a molecule changing in periodic manner with internal motion of the molecule. The time for a one-period duration is called *oscillation time* of a molecule as a whole. Notice that such type of description would be available from a solution of the time-dependent Schroedinger equation for a molecule. Because of technical problems, in practice such solutions have not been available until now. Therefore, a simplified model is still being looked for practical use.

In order to illustrate the heuristic and practical value of the chemical information, let us imagine the following computer experiment using virtual reality well known in modern computer science. Let us imagine a given molecule as a ''black box'' with a finite number of inputs/outputs representing functional groups

of the molecule. Let us assume that one of the inputs/outputs should be active in a desired reaction with another molecule. The activity means that the best momentary electron density distribution on the chosen functional group should be achieved at the moment of reaction. Let us assume also that we have an appropriate clock to measure time and ability to observe the best momentary electron density (named *the reactivity impulse*) in inputs/outputs, e.g., in a form of light flash. Now, we can go into the molecule, as it is possible in modern computer experiments. Just at the moment when we will see the first impulse in the chosen input/output, we start to measure time. After a period of time, we see a flash on another input/output in another point of the molecule, then on another etc., until we will observe the second impulse in the chosen input. The period of time when the second impulse appears is named the oscillation time of the molecule. If we will continue the experiment we would see the same sequence of impulses appear in different points in space in a different time. There is a reason why we can treat the chemical information carried by molecule as the space–time signals, which can be read out by another molecule at supramolecular level. What will be, if an observer posses different ability to see changes of momentary electron density distribution, e.g., the changes in time no shorter than characteristic time of conformational changes or no longer than the time of rotation? Different information will be obtained. In the case of the dynamic molecular recognition, the information available for a molecule depends on time of meeting with another molecule carried out the information.

3.2. Description of IOM

In the simplest case of diatomic molecule AB the momentary electron density distribution in the AB changes during stretching vibrational movement and the oscillation time of the molecule is equal to the vibrational period of the A–B vibrator. For a linear triatomic molecule ABC, e.g., the CO_2 molecule, the momentary electron density changes during the symmetric and asymmetric stretching modes and the bending mode. As the vibrations are periodical, there is also the oscillation time characteristic for the molecule.

The IOM generalised such considerations treating the reactant molecule and the catalytic center as sets of their vibrators. In a description of time-requirement for synchronisation of the best momentary electron density distributions in the reactant and the centre, the frequencies of the modes are used as the primary molecular parameters. The best distribution is named *the reactivity impulse*. In practice, the moment of appearance of the impulse in a reactant (or in a catalytic center) means that in each of considered vibrators of the reactant (or of the center) the best momentary electron density distributions appear at the same time. The electron density distribution in a vibrator changes during its vibrational movement, and appears periodically with consecutive vibrations. These momentary distributions can be related to momentary bond length in a considered vibrator during its stretching movement (or the value of an angle — for bending mode) and time of appearance can be connected with its vibrational period.

The scheme of the procedure for a simple reaction of two diatomic molecules is presented in Fig. 6. Notice that for a system of two (or more) molecules it is necessary to introduce the system time. It means that the moment $t = 0$ as the beginning moment of measure of the system time must be defined. In practice, for the models in heterogeneous catalysis, the moment just after adsorption of a reactant molecule on a catalytic center is assumed to be $t = 0$, while for the models in enzyme or in homogeneous catalysis — the moment of formation of reactant–catalyst complex are assumed. For such a well-defined moment, it is easy to define the beginning momentary states of the reactant and of the center. Indeed, at the moment of adsorption (or formation of the complex) the momentary states

$$A \text{----} B \quad + \quad C \text{-----} D \quad = ABC \quad + D$$

A---1------B
A--0.5---B   0.25 T_{AB}
A-0-B   0.5 T_{AB}
A--0.5---B   0.75 T_{AB}
A----1------B T_{AB}

time

C-0--D

C--0.5---D

C------1------D 0.5 T_{CD}

C--0.5---D

C-0--D

Assumed reactivity IMPULSES : FOR AB A-0--B ; FOR CD C------1------D
Situation at assumed   t=0 (the moment when we start to measure time in the system (AB ; CD)): A---1-------B; C-0--D

Impulse A-0--B appears at the discrete moments $t_{AB}= 0.5\, T_{AB} + n_{AB}\, T_{AB}$

Impulse C------1------D appears at the discrete moments $t_{CD}= 0.5\, T_{CD} + n_{CD}\, T_{CD}$

TIME CONDITION FOR THE REACTION TO OCCUR: $t_{AB}= t_{CD}= t_{SYN} = 0.5\, T_{AB} + n_{AB}\, T_{AB} = 0.5\, T_{CD}+ n_{CD}\, T_{CD}$

INSTEAD OF T WE USE   WAVENUMBERS (v [cm^{-1}]): $T= 1/\,w = 1/\,vc$; $T= 1/v$ (TIME UNIT: $1/c=1/3*10^{-10}$ s); w -frequency

$$t_{SYN} =(0.5 + n_{AB})/\, v_{AB} = (0.5 + n_{CD})/\, v_{CD}$$

FOR j (j=2 -25) OSCILLATORS CONSIDERED IN THE MODEL WE HAVE j EQUATIONS :

$$t_{SYN} = (w_1 + k_1 * n_1) / v_1 = (w_2 + k_2 * n_2) / v_2 = \ldots = (w_j + k_j * n_j) / v_j$$

WHERE: w (0, 0.25, 0.5, 0.75) -first appearance of the impulse; k (0.5, 1) - parameter describing if during one full vibration the
impulse appears two times (k=0.5) or once (k=1) ; n- natural number (number of vibrations)
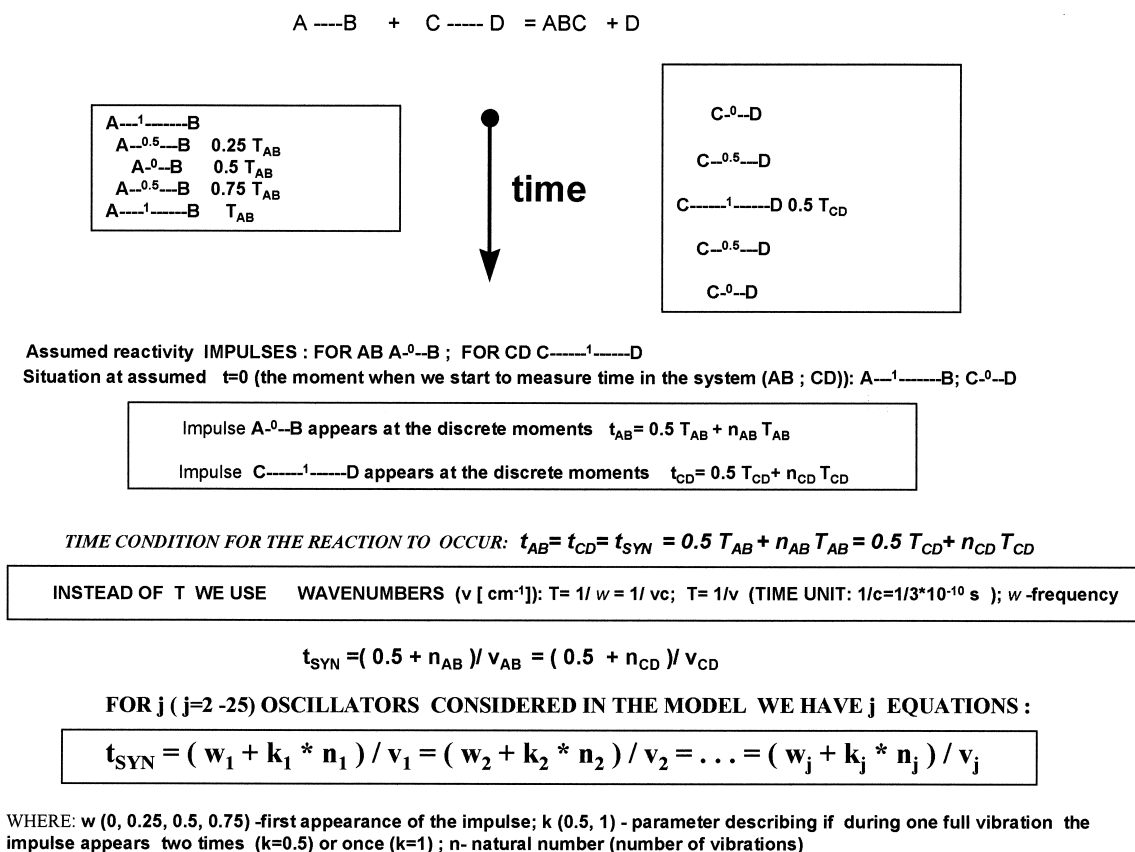
Fig. 6. The scheme of procedure uses in the IOM. The assumed impulses and beginning states result from analysis of a mechanism of a desired reaction in a considered catalytic reaction system.

of vibrators of the reactant and of the centre should be the best from the point of the adsorption (or of the complex formation). Therefore, in each particular catalytic system one can describe the momentary bonds length (or angles) at $t = 0$. Next, for the assumed mechanism of a considered reaction, the reactivity impulses of reactant and the centre can be described, in the sense of the bonds length and angles. Using the vibrational period for each of the considered vibrators, the system time of the first appearances of the impulses may be defined. Last but not least, the condition for synchronisation of the reactant and of the centre impulses can be formulated.

The IOM is used as a tool for calculation of time requirements which must be fulfilled for catalytic reaction to occur. It is assumed that the

reaction runs when the favourable distributions of the electron density in the reacting molecule and in the catalytic center appear at the same time — named the synchronisation time. The periodical appearance (named *oscillation*) of the reactivity impulse is closely connected with the electron density redistribution during the vibrations of reacting molecules and the catalytic center. Therefore, the vibrational modes of the reacting system are considered to be primary parameters describing the modeled system. These time parameters (vibrational periods) contain also information on energy, chemical composition and geometry of the vibrators microenvironment. The use of such primary parameters instead of a set of parameters describing separately all above-mentioned information simplifies calculation of the time requirements

in the IOM. As a result of IOM calculations, one obtains possible set of vibrational ranges within which synchronisation of the favourable distribution of the electron density in the reactant and in the center can be reached during the vibrations of the molecule and the catalytic center.

3.3. Methodology in IOM approach

In practice, the following steps are used in the IOM approach:

- choice of a mechanism of a considered catalytic reaction proposed in literature,
- analysis of the mechanism in order to define:
  ◦ a set of important vibrators in reacting molecule;
  ◦ a set of important vibrators in catalytic center
  ◦ reactivity impulses in the reactant and in the center,
- choice of the moment $t = 0$ of the system time scale,
- the distribution of the electron density in the reactant and in the center at $t = 0$,
- the time of synchronisation of the reactivity impulses of the reactant and the center (see Fig. 6),
- choice of frequency ranges for the defined important vibrators for use in calculation,
  ◦ analysis of appropriate available experimental ranges,
  ◦ auxiliary classical quantum chemistry calculation in order to look for tendencies of changes in frequencies with changing of metals and/or ligands in catalyst,
  ◦ expanding of the experimental ranges to lower and higher frequencies.

It must be pointed out that the IOM approach bases on assumed ranges of the frequencies (expanded experimental ranges rather than calculated ones). From the mathematical point of view, the IOM calculation means, in fact, fit-ting, step by step (usually the step $= 0.01 \text{ cm}^{-1}$), values of wavenumbers and numbers of consecutive vibrations with the synchronisation equations (see Fig. 6). The appropriate software for such calculation for personal computer was developed (the program IOMO) by Jamróz [47]. The computation time on PC Pentium II is from a few second to a few hours, depends on numbers of chosen vibrators (in practice 2–25); cases of assumed states at $t = 0$ and phases of vibrations. The latter number follows from the fact that if at the moment $t = 0$, the momentary length of a considered bond should be equal to the equilibrium length, such situation appears two times during one full vibration. One moment is when the vibration is during expansion (this phase was designated as R), the second — during contraction (the phase K). The both phases are taken into account in the calculation for each chosen vibrator which at the $t = 0$ is in such situation.

As the result of IOM calculation, for each of considered vibrator in the assumed range, sets of subranges fulfilling the synchronisation condition are obtained. These subranges are usually shifted in comparison to experimental spectra obtain separately for reactant and catalyst. These values in shifts contain information both about necessary chemical changes (e.g., change of metal in metal–oxygen vibrator) and about the force constants in the considered catalytic system (reactant + center), i.e., information on potential field, which should be in the catalytic system in order to fulfil the synchronisation conditions. Among sets of subranges for the chosen vibrators, there are such which can be assigned to known catalysts, and such which can be treated as new unknown catalysts. The latter sets are receipts for design of new catalytic molecular devices. Examples of practical use of the IOM will be presented in the next paragraph of this paper.

One of the most important characteristics of industrial catalyst is its selectivity. According to the IOM approach, selectivity at molecular level can be connected with the synchronisation time.

It is assumed that a reactant molecule in a same given state at $t = 0$ has different reactivity impulses for a desired reaction path A and a reaction path B. Differences between the impulses cause different synchronisation conditions along path A and path B. Using the IOMO program one can compute these conditions, for an assumed period of time justified from the point of view of the consideration of residence time of a reactant molecule on an active site and the lifetime of excited molecule [28].

The results from the IOMO calculations are sets of wavenumber ranges for the selected vibrational modes, are used as input data in the program IOMAB [48], developed by Jamróz, to determine a selectivity of choice of one from two possible (A or B) paths. The program IOMAB finds subsets of the ranges, where the synchronisation for only one way is possible (A or B) and the subsets, where synchronisation for both paths is possible. In the later case IOMAB distinguishes a case when the synchronisation time for the A path is shorter than for path B (AB case) and a case when the time for path B is the shorter one (BA case). The selectivity of choice of path A is calculated in the program IOMAB from the following formula:

$$Sa = (A + AB + BA)100$$
$$/\left[A + B + 2(AB + BA)\right] \tag{5}$$

where: A, B, AB, BA — sums of the width (in wavenumbers) of ranges where the above described cases of synchronisation are possible. Detailed description of methodology, set of programs for PC and some examples of practical use of the IOM were recently published [49].

The IOM method seems to be a more general approach than the well known resonance concept in catalysis developed mostly by Russian theoreticians [50]. In the resonance concept, the importance of fitting of appropriate frequencies of a reactant vibrator and of a vibrator of catalyst was pointed out. Indeed, in particular cases, when the first reactivity impulses of a reactant and of a catalytic center appear at the beginning

moment $t = 0$ and only one vibrator in a reactant molecule and only one vibrator in a catalytic center are important from the point of view of the synchronisation conditions, the full analogy of the IOM model and the resonance concept occurs. Recently, Larsson [16,17] has developed the resonance concept from the point of view of selective energy transfer (the SET model). Efforts have been made [51] to combine the SET model and the IOM in order to obtain energy and time requirements common description of catalysis at molecular level.

The IOM approach was used until now for analysis of more than 20 elementary reaction paths. In all cases good agreements between available experimental data, as well as good prediction were found. In the simplest cases, results of auxiliary calculations with standard quantum chemistry methods were complementary with the results obtained in the IOM calculations. Such complex approach combining both the IOM and the quantum chemistry methods makes possible more detail understanding of the time, geometry and energy aspects of a considered catalytic reaction as it will be shown below on the examples of practical application.

4. Examples of application of the IOM

The IOM approach has been used first time for modeling of the isomerization of 1-butene on ZnO [52]. The mechanism proposed by Chang et al. [53] was used. The results of computations using the IOM show that in the range of characteristic Zn−O surface vibrations of ZnO [54] there are centers, which transform π adsorbed 1-butene into π-allyl species. In the case of polycrystalline specimen of ZnO, the characteristic surface modes in the 600–700 cm^{-1} range are mainly microscopic in character and the characteristic triplet with maximum at 675 cm^{-1} is clearly visible [54]. The computed with IOM values of wavenumbers, for which the synchronisation conditions are fulfilled, were found in

the 689–668 cm^{-1}, in the 647–641 cm^{-1} and in the 631–641 cm^{-1} sub-ranges. The most profitable seemed to be the wavenumbers near 680 cm^{-1}, i.e., near the observed experimentally maximum [54] of the characteristic surface modes. These results were compared with those obtained for other oxides (Cr_2O_3 with different Cr coordination numbers and with Fe_2O_3). The optimum sub-ranges were found and the comparison seemed to show that from the point of view of the IOM on the optimum centers, the shortest time of synchronisation is for ZnO and the longest is for Fe_2O_3. In the next elementary step there are Zn−O−H centers, which are able to favour selectively increasing *cis/trans* ratios (e.g., for wavenumbers of the Zn−OH mode near 580 cm^{-1}) or decreasing it (e.g., for wavenumbers of the Zn−OH mode near 658–648 cm^{-1}). In order to control a high value of the *cis/trans* ratio one has to obtain, e.g., high participation of the Zn−OH mode near 580 cm^{-1} in the distribution of surface sites of ZnO.

4.1. Catalytic decomposition of HCOOH on metal oxides

This example of the IOM application will be described step by step in order to illustrate how the model is constructed in the particular case of simple reactant molecule and simple reactions occurring on heterogeneous catalysts. These decomposition reactions have been also studied using the SET model and auxiliary quantum chemistry calculations.

4.1.1. Choice of a mechanism

The decomposition of formic acid over heterogeneous catalysts is a classical reaction, which has been studied by both experimentalists and theoreticians for many years. Many problems concerning this reaction have been highlighted, but there is still no agreement about its mechanism. The main goal of recent studies on the reaction is to find the most selective catalyst for the dehydrogenation of formic acid. To achieve this goal, one can try to understand the chemistry of a particular oxide having a variety of surface sites. However, the chemistry of the surface species appears to be very complex [55] because of a variety of products observed in experiments with different oxides and for different conditions. On the other hand, there are experimental evidence that, in particular conditions, high selectivity of one from the two dominant reactions — dehydrogenation or dehydration ones — can be achieved [56–59]. Switchover of reaction paths in such selective decomposition is postulated [56–59]. For the dehydration reaction, the unimolecular decomposition of formates at the surface is rate controlling. Below 500 K the catalytic dehydrogenation reaction is suggested to proceed as a bimolecular process of a formate ion adsorbed on TiO_2 and formic acid molecule from gas phase. Therefore, unimolecular and bimolecular mechanisms should be considered separately, looking for the best selective catalyst with the IOM.

It is commonly considered [60] that the formate ion is the reactive intermediate in the decomposition reactions. Three different forms of the formate ion adsorbed on metal oxides surface have to be taken into account, namely monodentate, bidentate and bridged [61]. Thus, for each of the mechanism the three forms must be separately considered for two reaction paths, i.e., for the dehydrogenation path (named path A) and for the dehydration path (path B). Below, the next steps of the IOM procedure will be presented only for the bidentate form of the adsorbed formate ion.

Notice that the IOM calculation were made in order to look for appropriate conditions for the dehydrogenation reaction to occur at molecular level and not to explain catalytic behaviour of a particular known metal oxide catalyst.

4.1.2. Analysis of the unimolecular mechanism

As it was described above, it is necessary to define first sets of important vibrators in the formic ion and on surface of metal oxide catalysts, next the reactivity impulses of the formic

ion and the active surface site defined with the chosen important vibrators. In order to introduce the system time one has to choice the moment $t = 0$ and describe the electron density in the formic ion and in the active site at the moment. Last not least, the conditions of synchronisation of the reactivity impulses in the system time can be formulated.

4.1.3. The set of important vibrators in bidentate form of adsorbed formate ion

The set of following six vibrators are taken into account in the model:

1. $\nu1$ — OCO asymmetric stretching mode
2. $\nu2$ — OCO symmetric stretching mode
3. $\nu3$ — OCO bending mode
4. $\nu4$ — HC stretching mode
5. $\nu5$ — HCO bending mode
6. $\nu6$ — CO–metal stretching mode

4.1.4. The set of important vibrators in the catalytic center

The two vibrators are considered in the model:

1. $\nu7$ — O−H surface group
2. $\nu8$ — metal–oxygen surface vibrations

4.1.5. The reactivity impulses for the dehydrogenation reaction (Path A)

For path A, the most favourable distribution of electron density in the formate ion is the one that prefers the highest density on the H of the H−COO$^-$ ion. It appears in the moment when on the C atom the density is also very high. This situation relates to the maximum overlap of orbitals of oxygen atoms with orbitals of carbon in the OCO bonds system. The most favourable distribution of electron density in the catalytic center for the dehydrogenation reaction to occur is that with the lowest density on the H of the surface group O−H related to the maximum overlap of orbitals of the metal and lattice oxygen atoms and the minimum overlap be-

tween orbitals of metal and formic oxygen atoms.

The momentary distribution of the electron density can be related to the momentary lengths of the bonds in the different stage of the vibration. In practice, in the IOM approach only three particular partial charge distributions are used: the two extreme ones and the equilibrium distribution corresponding to three bond lengths, namely the shortest (named stage 0), the longest (stage 1) and the equilibrium length (stage 0.5). Taking into account the above consideration and using the proposed notation the reactivity impulses for path A are defined as:

1. $\nu1$ — OCO asymmetric stretching mode: 0; 1
2. $\nu2$ — OCO symmetric stretching mode: 0
3. $\nu3$ — OCO bending mode: the smallest angle OCO
4. $\nu4$ — HC stretching mode: 1
5. $\nu5$ — HCO bending mode: the largest angle HCO
6. $\nu6$ — CO–metal stretching mode: 1
7. $\nu7$ — O−H surface group: 1
8. $\nu8$ — metal–oxygen surface vibrations: 0

4.1.6. The reactivity impulses for the dehydration reaction (path B)

For path B the most favourable distribution of the electron density in the formate ion is the one that prefers the lowest density on the H of the H−COO$^-$ ion. The best distribution in the catalytic center is that with the lowest density on the H of the surface group O−H. In full analogy to the above consideration, the definition of the reactivity impulses for the dehydration reaction are the following:

1. $\nu1$ — OCO asymmetric stretching mode: 1; 0
2. $\nu2$ — OCO symmetric stretching mode: 1
3. $\nu3$ — OCO bending mode: the largest angle OCO
4. $\nu4$ — HC stretching mode: 1

5. $\nu5$ — HCO bending mode: the largest angle HCO
6. $\nu6$ — CO–metal stretching mode: 1
7. $\nu7$ — O−H surface group: 1
8. $\nu8$ — metal–oxygen surface vibrations: 1

4.1.7. Choice of the moment t = 0 of the system time scale

The moment $t = 0$ is defined as the moment just after chemisorption of formic acid on the surface of metal oxide.

4.1.8. The distribution of electron density in the formate ion and in the center at t = 0

The most favourable distribution for the bidentate form is that with the same electron density on both formate oxygen atoms. The same lengths of C−O bonds relate to this distribution. Thus, the moment when the stage 0.5 of the bond lengths during asymmetric and symmetric stretching vibrations should be assumed at the beginning moment $t = 0$. For the catalytic center, the maximum density on surface oxygen where hydroxyl group just formed and the minimum density on the metal atoms where formate oxygen–metal bonds just formed, should be assumed.

Thus, the following situation at the beginning moment $t = 0$ was assumed:

1. $\nu1$ — OCO asymmetric stretching mode: 0.5; 0.5
2. $\nu2$ — OCO symmetric stretching mode: 0.5
3. $\nu3$ — OCO bending mode: the largest angle OCO
4. $\nu4$ — HC stretching mode: 0
5. $\nu5$ — HCO bending mode: the smallest angle HCO
6. $\nu6$ — CO–metal stretching mode: 1
7. $\nu7$ — O−H surface group: 1
8. $\nu8$ — metal–oxygen surface vibrations: 1

Notice that for the bonds just formed (vibrators 6 and 7), the longest lengths (i.e., in the proposed notation-stages 1) were assumed.

4.1.9. The time of synchronisation of the reactivity impulses of the formate ion and the center

According to the IOM, the reactivity impulse appears at discrete moments of the system time (see Fig. 6). In order to formulate the equation it is necessary to know the time of first appearance of the impulse for each of considered vibrators. For instance, for the vibrator $\nu4$ (HC stretching mode) it was assumed that at $t = 0$ it is in the stage 0, while in the reactivity impulse for path A it should be in the stage 1. It means that, after the time equal to half of its vibrational period, the vibrator first time will appear at appropriate stage and this stage will next appear periodically at discrete moments after each consecutive vibrations.

As it was mentioned before, if at the beginning moment the assumed momentary stage is 0.5, it is necessary to consider two cases for the phase of the vibration: the phase R when the vibration is during expansion and the phase K corresponds to contraction of the vibration. There are the two modes in the considered model, namely, $\nu1$ and $\nu2$ in such a situation. For instance, for the vibrator $\nu2$ (OCO symmetric stretching mode) it was assumed that at $t = 0$ it is in the stage 0.5, while in the reactivity impulse for path A it should be in stage 0. It means that (see also Fig. 6), after the time equals to 0.25 of its vibrational period — if the vibrator is during contraction (phase K) — or after the time equals to 0.75 (phase R), the vibrator will appear time at the appropriate stage 0, and this stage will next appear periodically at discrete moments after each consecutive vibrations. Four combinations of the phases for each of the paths were considered (RR, RK, KR, KK).

The discrete moments of appearance of the desired distribution of electron density for each of the considered bonds are determined using the formula presented in Fig. 6. If the distributions will appear at the same time t_f for all of the six formate ion vibrators, the time t_f is the time of appearance of reactivity impulse of the formate ion. In full analogy the time t_c is the

time of appearance of the impulse of the center. Synchronisation of these impulses means $t_f = t_c$. In practice, the eight equations (eight vibrators) constitute the IOM model for, e.g., the RR phase combination for the bidentate form of formate ion decomposition towards dehydrogenation for unimolecular mechanism. Because of the four combinations of phases and the two paths, we have used eight sets of eight equations for calculation of the unimolecular decomposition of formate ion chemisorbed in the bidentate form on metal oxide catalysts. The appropriate sets of equations are collected in Table 1.

4.1.10. Choice of frequencies ranges for use in calculation

Based on literature data, the following wavenumber ranges are chosen for the computation:

1. $\nu1$ — OCO asymmetric stretching mode: 1679–1521 cm^{-1};
2. $\nu2$ — OCO symmetric stretching mode: 1399–1301 cm^{-1};
3. $\nu3$ — OCO bending mode: 910–701 cm^{-1};
4. $\nu4$ — HC stretching mode: 2980–2820 cm^{-1};
5. $\nu5$ — HCO bending mode: 1099–1001 cm^{-1};
6. $\nu6$ — CO–metal stretching mode: 1199–1080 cm^{-1};
7. $\nu7$ — O–H surface group: 3499–3201 cm^{-1};
8. $\nu8$ — metal–oxygen surface vibrations: 799–351 cm^{-1}.

4.1.11. Discussion

In our recent paper [62], using the selective energy transfer (SET) model, it was found, for the dehydration reaction the asymmetric stretching O–C–O mode, while for the dehydrogenation reaction the O–C–O in plane bending mode are those which must be excited for the reactions to occur. The results of modeling, partly presented above, of the same reactions with the IOM, shown that only for bidentate form for the combination RK and KK (the phases of the $\nu1$ mode — asymmetric stretching OCO and of the $\nu2$ mode — symmetric stretching OCO), the selectivities for dehydrogenation reaction are higher than 50%. The selectivity 61% is obtained for the RK combination, i.e., for the initial situation when one of the C–O bonds, viz., the one near the surface OH group is expanded in the $\nu1$ mode and the O–C–O bonds contract in the $\nu2$ mode. For the situation KK when the above mentioned bonds are contracting the selectivity is 59%. All of the other situations result in selectivity of the dehydrogenation reaction lower than 50%, i.e., the dehydration reaction is preferred. In the statistic picture, i.e., for the averaged, for the all considered formate ion forms, selectivity in the most important modes for the dehydrogenation reaction are the OCO bending mode in the formate and the O–H stretching mode on catalyst surface while for the dehydration reaction — the asymmetric stretching mode OCO in the adsorbed formate and the metal–oxide stretching mode on oxide catalysts. The following best subranges of wavenumbers of vibrators, taken into account in the IOM for the dehydrogenation reaction, were found as the result of the calculation:

1. $\nu1$ — OCO asymmetric stretching mode: 1580–1565 cm^{-1};
2. $\nu2$ — OCO symmetric stretching mode: 1325–1310 cm^{-1};
3. $\nu3$ — OCO bending mode: 900–860; 760–720 cm^{-1};
4. $\nu4$ — HC stretching mode: 2980–2970; 2850–2830 cm^{-1};
5. $\nu5$ — HCO bending mode: 1050–1040 cm^{-1};
6. $\nu6$ — CO–metal stretching mode: 1165–1150; 1130–1120 cm^{-1};
7. $\nu7$ — O–H surface group: 3499–3460; 3260–3200 cm^{-1};

Table 1
The IOM model for the reactions of HCOOH decomposition (The bidentate form, unimolecular mechanism)

Vibrator phases	1	2	3	4	5	6	7	8
The dehydrogenation reaction (path A)								
RR	$(0.75+n1)/v1$	$(0.75+n2)/v2$	$(0.5+n3)/v3$	$(0.5+n4)/v4$	$(0.5+n5)/v5$	$(0+n6)/v6$	$(0+n7)/v7$	$(0+n8)/v8$
RK	$(0.75+n1)/v1$	$(0.25+n2)/v2$	$(0.5+n3)/v3$	$(0.5+n4)/v4$	$(0.5+n5)/v5$	$(0+n6)/v6$	$(0+n7)/v7$	$(0+n8)/v8$
KR	$(0.25+n1)/v1$	$(0.75+n2)/v2$	$(0.5+n3)/v3$	$(0.5+n4)/v4$	$(0.5+n5)/v5$	$(0+n6)/v6$	$(0+n7)/v7$	$(0+n8)/v8$
KK	$(0.25+n1)/v1$	$(0.25+n2)/v2$	$(0.5+n3)/v3$	$(0.5+n4)/v4$	$(0.5+n5)/v5$	$(0+n6)/v6$	$(0+n7)/v7$	$(0+n8)/v8$
The dehydration reaction (path B)								
RR	$(0.25+n1)/v1$	$(0.25+n2)/v2$	$(0+n3)/v3$	$(0.5+n4)/v4$	$(0.5+n5)/v5$	$(0+n6)/v6$	$(0+n7)/v7$	$(0+n8)/v8$
RK	$(0.25+n1)/v1$	$(0.75+n2)/v2$	$(0+n3)/v3$	$(0.5+n4)/v4$	$(0.5+n5)/v5$	$(0+n6)/v6$	$(0+n7)/v7$	$(0+n8)/v8$
KR	$(0.75+n1)/v1$	$(0.25+n2)/v2$	$(0+n3)/v3$	$(0.5+n4)/v4$	$(0.5+n5)/v5$	$(0+n6)/v6$	$(0+n7)/v7$	$(0+n8)/v8$
KK	$(0.75+n1)/v1$	$(0.75+n2)/v2$	$(0+n3)/v3$	$(0.5+n4)/v4$	$(0.5+n5)/v5$	$(0+n6)/v6$	$(0+n7)/v7$	$(0+n8)/v8$

8. $\nu 8$ — metal–oxygen surface vibrations: 750–720 (TiO$_2$); 670–660 (SnO$_2$; NiO); 580–550 (Fe$_2$O$_3$; Cr$_2$O$_3$); 420–400 cm^{-1} (CuO; Cr$_2$O$_3$; MnO$_2$)

The assigned metal oxides for the $\nu 8$ mode were proposed based on the spectroscopic data collected by Davidov [63]. More detail discussion of the results of IOM approach to the unimolecular decomposition of formic acid on metal oxide catalyst is presented in our recent paper [64].

From the point of view of the IOM, looking for good catalyst it is need of spectroscopic characteristics of the metal oxide. As it was expected [64], in the statistic picture of averaged values of the selectivity, there are few oxides with high selectivity to the dehydrogenation reaction (the averaged values is near 50%). It was shown that the selectivity strongly depends on the form of adsorbed formate ion. It was interesting to compare the unimolecular mechanism and bimolecular mechanism of the catalytic decomposition of HCOOH.

4.1.12. Results of IOM calculation for the bimolecular mechanism

According to the mechanism proposed in the papers [56–59] for the bimolecular dehydrogenation reaction the lateral coulombic (acid–base) interaction between H$^{\delta-}$ of HCOO$_s$ (adsorbed on the TiO$_2$ surface) and H$^+$ of HCOO–H is more important than the vertical coulombic (acid–base) interaction between HCOO$_s$ and Ti^{4+}. Formate ions on TiO$_2$ (110) form a monolayer ordered in a (2∗1) periodicity. The C–H bond of a formate is normal to the surface, while the O–C–O plane is parallel to the [001] axis. According to the cited authors, it is reasonable that the formates are adsorbed on TiO$_2$ (110) in a bridged form rather than bidentate or monodentate forms.

A set of 13 vibrational modes was taken [65] into account in the IOM calculation. The six internal modes of formate ion adsorbed on the surface, OH surface group, the bonds between oxygen in formate and metal, metal–oxygen surface vibrational mode as well as the five modes in a molecule of formic acid interacting by two hydrogen bonds with the formate ion constitute the set. The two hydrogen bonds were suggested [66] for the most stable diformate anion and confirmed with ab initio calculations of the HCOOH · HCOO$^-$ system [67–70]. In full analogy to the unimolecular mechanism, the IOM calculations were made and the results are presented in the paper [65]. Here only the comparison between the unimolecular and bimolecular mechanisms will be discussed.

4.1.13. Comparison of the selectivity for unimolecular and bimolecular mechanisms

In contrast to the unimolecular mechanism, bidentate species where the only with selectivities for dehydrogenation reaction that are higher than 50%, in the bimolecular mechanism also the averaged selectivity for formate ions adsorbed as monodentate or bridged forms is 60% in comparison to 42% in the former mechanism. These results are connected with changes of modes, which are the most important in the reaction. In fact, for the bidentate form the OCO bending mode in formate and the O–H surface stretching mode are most important in the unimolecular mechanism, while in the bimolecular mechanism for monodentate and bridged forms the most important modes are the O–C stretching one in the formate, the OCO bending mode in HCOOH and the metal–oxygen stretching mode on catalyst surface. In the latter mechanism, for bidentate adsorbed form, the selectivity strongly depends on the combination of the phases and is highest for the combination RRR (68%) — in comparison to the highest selectivity 61% for the RK combination in unimolecular mechanism — and lowest for the KKK combination (49%). In the combination RRR the most important modes are the symmetric stretching O–C–O and the OCO bending modes in formate and the metal–oxygen stretching mode on catalyst surface. The other important

modes are, in order, the HCO bending mode in formate, the OC−O stretching, the OCO bending, the OC=O stretching and the HCOO−H stretching modes in the acid. These changes of modes of most importance in the bimolecular mechanism can be explained [65] from the point of view of the postulated [56–59] mechanism, which does not need big deformation of the OCO bond system in formate and uses as a source of acid proton formic acid, and not surface hydroxyl group on catalyst.

According to the IOM, even in the case of bidentate formate ion adsorbed on the catalyst oxide surface, one can expect very complex answers of the system in experiments with different oxides and for different conditions. In Fig. 7, the collected possible answers, dependent on the subranges of wavenumbers of the metal–oxygen stretching mode on catalyst surface, are presented. It seems that the disagreement in literature [55] on mechanisms and selectivity of the catalytic decomposition of HCOOH one can try to explain taking into account the presented on Fig. 7 dependence — for the three possible adsorbed forms of formate ion — between the possible mechanism and the possible subranges of wavenumbers of the metal–oxygen stretching mode on real catalyst surface. Notice that in the above-described IOM approach the time requirements for only two main decompo-

sition reactions (the dehydrogenation and the dehydration) were considered.

4.2. The reaction of carbon dioxide with dimethylamine

The practical aspects of the synthesis of organic carbamates from carbon dioxide and an amine, as a route competitive to harmful process using phosgene, are well known [71]. Since the reaction between CO_2 and amine may be the rate-limiting step, extensive studies have been carried out into the kinetics of the reaction [72–76]. A few theoretical studies [77–79] have also been carried out. The mechanisms of the reaction, found theoretically [77–79] and experimentally [72–76], are inconsistent. The general consensus is that the reaction is of first order with respect to CO_2. However, the reaction order with respect to an amine ranges from one to two, whereby different reaction schemes are implied. The theoretical investigations, based on carbon dioxide: amine (1:1) reaction system [77–79] result in 3–4 times greater calculated activation energy than the experimental values. In our recent paper [80] it was shown that the ab initio RHF/3-21G modeling, if the reaction is assumed to occur in the present of a second amine molecule (1:2 system), leads to the calcu-
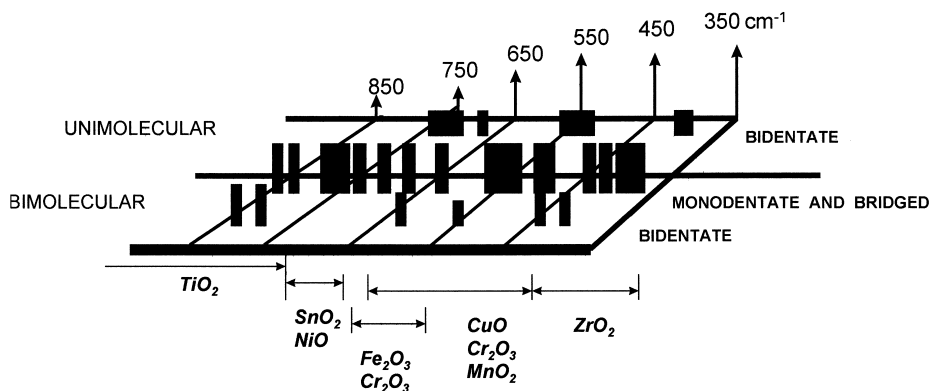

Fig. 7. Calculated with the IOM subranges of wavenumbers of the metal–oxygen stretching mode of metal oxides, where the synchronisation for the formic acid decomposition toward the dehydrogenation reaction is possible. The calculation was made for unimolecular and bimolecular mechanisms, for bidentate, monodentate and bridged species of adsorbed formate ion. The assigned metal oxides for the mode were proposed based on the spectroscopic data collected by Davidov [63].

lated activation energy fairly close to that found experimentally. The decrease of the activation energy results from the presence of the second amine, which serves as a catalyst in proton transfer process.

In this particular example of a relative simple reaction system, for which the quantum chemistry ab initio calculations were possible, a comparison between results of these calculations and results of the IOM approach can be made.

In the IOM approach [81], two reaction systems were considered. The first one, where the reaction starts from the bimolecular intermolecular complex, viz., one carbon dioxide molecule and one amine molecule. The second system, where the reaction starts from the trimolecular complex, i.e., one carbon dioxide and two amine molecules. The optimal geometries of the complexes have been found at the RHF/3-21G level [80], while the vibrational modes of each substrate and product have been studied at the B3PW91/6-31G** level [82]. It was assumed that both systems could change either toward free substrates or toward carbamate. In the first system seven modes are taken into account: the three modes in CO_2 and the four following modes in the amine: the CN1H bending, the N1−H stretching, the CN1C bending and the CN1C symmetric stretching modes. In the trimolecular complex system the same modes and additionally four: the CN2H bending, the N2−H stretching, the CN2C bending and the CN2C symmetric stretching modes in the second amine are considered (N1 and N2 notions mean the first and the second amine, respectively).

The results of IOM calculations shown that in the both considered systems the selectivity towards carbamate formation is larger than towards complex dissociation, i.e., the calculated with quantum chemistry optimal geometries seem to be optimal for the reaction to occur. The averaged selectivity toward carbamate formation for the bimolecular mechanism is equal to 61%, while 80% for the trimolecular. It confirms the conclusion [80] from the quantum chemistry modeling.

For the bimolecular mechanism, the most important is the CN1H bending mode (selectivity 72%). Also important are the CN1H bending mode and the OCO bending mode (selectivity exceeding 63%). The O−C−O asymmetric stretching mode (selectivity 50%) exhibits the smallest selectivity toward the carbamate formation. For the trimolecular mechanism, the modes that most strongly favour the carbamate formation are the bending modes: the OCO mode (selectivity close to 100%), the CN1H mode in the first amine and the CN2C mode in the second amine with identical selectivities of 90%. As in the bimolecular mechanism, the O−C−O asymmetric stretching mode (selectivity 50%) exhibits the smallest selectivity toward the carbamate formation.

It is easy to understand why the bending OCO vibration is very important to the course of the reaction: in the carbamic acid product, the OCO moiety is bent. In full analogy, in the first amine molecule the bending CN1H mode is significant because the CCNH tetrahedron is flattened in the product. Note that in the second amine molecule (serving as catalyst), the bending CN2H mode is of less importance (selectivity 77%) for the reaction. The significance of the CN2C mode of the second amine molecule can be seen in the proton transfer process from the first to the second amine, as it was found [80] in quantum chemistry modeling. Unexpected, the O−C−O asymmetric stretching vibration, which favours the asymmetry of the two C−O bonds, turned out to be not important for the reaction. This fact may indicate that the proton of the first amine jumps directly on the second amine molecule [80], rather than on the OCO moiety.

The predicted IOM profitable subrange of OCO bending mode wavenumber is 659–646 cm^{-1} (in the range 680–630 cm^{-1} assumed for calculation). The calculation at the B3PW91/6-31G** level [82] predicts, in the reacting system for the nondegenerated OCO bending modes, are two wavenumbers: 654 cm^{-1} and 570 cm^{-1}.

Thus, the IOM analysis seems to be in good agreement with our recent quantum chemical studies [80,82]. Note that these two methods are based on completely different criteria: the quantum chemical investigations refer to the minimal energy of the system, whereas the IOM verifies time requirements only. One can say that in this particular example of a relative simple reaction system, for which the quantum chemistry ab initio calculations were possible, the comparison between results of these calculations and results of the IOM approach clearly show that energy, geometry and time requirements for the catalytic reaction to occur, results in consistent description of catalysis from the point of a system view. One can also expect that in cases of much more complex catalytic reaction systems, for which the quantum chemistry ab initio methods are not possible to be used, the results of calculation with IOM approach can still be reasonable and the IOM can serve as the useful tool for design of new catalysts. An example of such application of IOM is presented below.

4.3. Cyclic carbonates formation in catalytic reaction between olefins, O_2, CO_2

This example of application of the IOM approach for modeling of rather complex reaction systems illustrates how profitable is the use of vibration modes as the primary molecular parameters in reasonable simplification of description of the complex systems. As it was mentioned before, frequency of vibrator contains information on its microenvironment (shifts of the frequency in different microenvironments). Therefore, it is not necessary to consider all modes in catalytic system, but only those vibrators which, e.g., are bonding directly with metal in metal complexes. Moreover, the example clearly indicates the possibility of identifying, through the vibration modes, proper ligands and metal systems that behave as selective homogeneous catalysts at the molecular level.

The formation of carbonates in direct synthesis from olefins, O_2, CO_2 has been studied from many years by Aresta et al. [83,84]. All the data concerning the experimental facts and proposed mechanisms used by the author of this paper in the IOM modeling based on these studies [85]. It was found [83,84] that the formation runs through three main steps. In the first one, the (η^2-dioxygen)–rhodium complex formates in the reaction of the rhodium complex with oxygen. In the second step, the reaction of CO_2 with the (η^2-dioxygen)–rhodium complex gives peroxo-carbonates, $L_nXRhOOC(O)O$, which are likely to be intermediates in both the olefin oxidation and carbonate formation reactions (the third step).

4.3.1. Formation of the peroxocarbonates

Recently, the mechanism of formation of Rh(III)–peroxocarbonates from CO_2 and $P_3ClRh(\eta^2-O_2)$ (P = phosphane) complexes has been investigated [86] to ascertain if the hetercumulene inserts into the O−O or the Rh−O bond of the $Rh(\eta^2-O_2)$ moiety. It was demonstrated that formation of peroxocarbonate occurs via insertion of CO_2 into the O−O bond of the O_2 molecule η^2-coordinated to Rh.

The IOM was applied [87,88] to the general case of the reaction of a six-coordinated dioxygen metal–complex with CO_2, in order to calculate selectivity of choice of the two possible pathways and to select metal-systems that behave according to the proposed [86] reaction mechanism. The considered reaction system contains 85 atoms and 91 bonds. Only 10 key vibration modes are taken into account. The three modes of CO_2 and seven modes characteristic of the metal system, namely the five stretching modes: the O−O; the O−M−O asymmetric and the O−M−O symmetric; the M−X (X = F, Cl, Br, I) and the M−L (L = P, N), and the two bending modes : the M(O−O) and the L−M−L. For path A (the O−O bond cleavage), the reactivity impulse is assumed to be the momentary state, when the symmetric (same length of both M−O bonds) minimum overlapping of the O−O bonding orbitals, and

minimum electron density at the metal centre appear. Conversely, path B (M−O bond cleavage) requires the maximum overlapping of the O−O bonding orbitals, asymmetry of the M−O bonds (that must be different in length), and maximum electron density at the metal centre. For both paths, the same reactivity impulse for the CO_2 molecule has been assumed, corresponding to a bent molecule (angle close to 133° [89]) with two quite different C−O bonds.

Four cases of the situation at the beginning moment ($t = 0$) differ in symmetries of the complex and of CO_2 molecule and eight possible phase combinations were taken into account in the IOM modeling. For each set of 10 equations (10 vibrators) calculations are made using three different ranges of wavenumbers corresponding to: (1) $M-{}^{16}O_2$ and ${}^{12}C{}^{16}O_2$; (2) $M-{}^{18}O_2$ and ${}^{12}C{}^{16}O_2$ and (3) $M-{}^{16}O_2$ and ${}^{12}C{}^{18}O_2$, in order to compare the experimental results [86] with those predicted by the IOM.

The result of the IOM calculation clearly show that the reaction takes place through the insertion of carbon dioxide into the O-O bonds, regardless of the initial case and phase combination. In fact, the averaged probability for such CO_2 insertion is well over 50% in almost all of possible cases considered and reaches a maximum of 98%. For a very limited number of selected ranges of vibrations the selectivity towards the insertion into the M−O bond can be as high as 75%, but confined to only very few of the 132 case (44 sets of 10 equations and the three different isotope labeling at oxygen) considered. More detail discussion is presented in the paper [87,88].

For each of the considered vibration modes of the peroxo-complex, the subranges of frequencies, for which the synchronisation for the path O−O is found, have been predicted with the IOM. It is interesting to note that all of the IR frequencies experimentally found [86] for the complex $Rh(O_2)P_3Cl$ (P = PEt_2Ph) that reacts via insertion of CO_2 into the O−O bond, are within 2 cm^{-1} with one of the set of calculated values.

The fact that both the theoretical and experimental results point at the CO_2 insertion into the O−O bond of the M−O_2 moiety validates the IOM approach as a potential tool for homogeneous catalyst design and finding the best metal system (metal centre and ligands) for catalytic applications.

The molecular structure, energetics and vibrations have been calculated [90], for the MO_2 moiety in the simplified $M(O_2)X(YH_3)_3$ (M = Rh,Co; X = F,Cl,Br,I; Y = P,N) complexes used as models for the $M(O_2)(PEt_2Ph)_3Cl$ homogeneous catalyst, in order to look for tendencies of changes of these properties with changing metals and ligands. The study was performed by using the RHF/3-21G**, B3PW91/6-31G** and PM3(tm) quantum chemical methods. The methods yielded the O−O distances consistent with the experimental values and similarly predicted the tendencies of geometrical parameters to change. The variation of the enthalpy of formation with the central metal atom, halogen and ligand seems to be in qualitative interconsistency, whereas changes in the MO_2 moiety frequencies, found at different levels, disagree substantially.

4.3.2. Reaction of peroxocarbonates with olefines

More than 100 atoms and 91 bonds constitute the reacting system. The four main pathways, namely formation of aldehyde, ketone, oxirane and carbonate are possible. Such picture is rather simplified and does not include possible secondary reactions and oxidation of solvent or ligand as well as the break of the C=C bond of olefin and consecutive reactions of products of the destruction. However, the picture is reasonable in the IOM modeling, where one has searched for optimal conditions for the desired reactions to occur.

The proposal probably set of possible reactions occurring in the considered chemical system is presented on a scheme (Fig. 8). In this scheme, a hypothetical transition state, common for all desired reactions (formation of aldehyde,
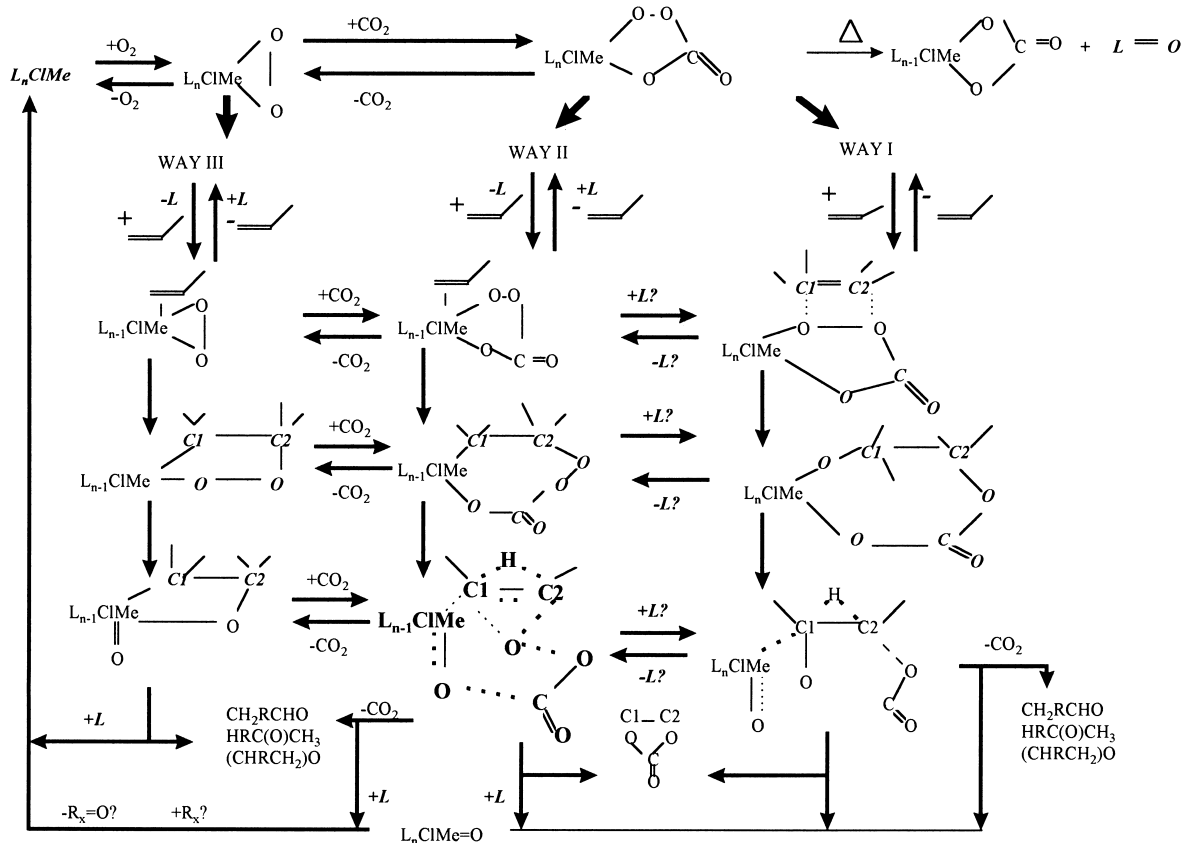
Fig. 8. The simplest set of possible reactions assumed [85] in the IOM procedure for preliminary analysis of the reacting system for cyclic carbonates formation in catalytic reaction between olefins, O_2, CO_2.

ketone, oxirane and carbonate) is distinguished. The assumption of one common initial state for the reactions results from analysis of the scheme, preliminary semiempirical calculation and suggestions from the experimental data [83,84,89, 91,92]. According to the scheme, the initial state can be formed either on the way I, starting from an attack of olefin on peroxocarbonate system or on the two other ways (II and III). The way I differ from the two latter ways in phases of vibrational motion of the two C−O bonds of C1OC2 moiety (see Fig. 8). If the initial state is formed on the way I the C1−O bond length (C1 is the carbon atom closer to Rh in the scheme) decreases (the phase K) while the C2−O bond length increases (the phase R). If the initial state is formed on the way II or III, the phases are

reversed. To distinguish these two different situations in the model, for the asymmetric stretching mode in the C1OC2 moiety the two different initial phases were taken into account (named combination (KR) and (RK), respectively).

The four main reactions can be divided into two pairs. The first pair — in which hydrogen transfer between olefin carbon atoms is necessary — contains alDehyde (named path D) and Ketone (path K) formation. The second one — with no hydrogen transfer — corresponds to Oxirane (the path O) and Carbonate (the path C) formation. Thus, the following two steps of choice were considered. In the first step, conditions for the hydrogen transfer and for the reactions without the transfer were defined (the choice of one of the pairs). In the second step

— separately for each of the pair — conditions for synchronisation for two paths (D or K) and (O or C) were considered.

Usually, the mechanism via metal hydride intermediate is proposed for the hydrogen transfer. From the point of view of the IOM, this mechanism needs the reactivity impulse, which has low electron density on the metal. In the case when the formation of the metal hydride is not possible (central metal atom fully coordinated) the mechanism like 1,3-suprafacial-hydrogen shift, proposed [93] for the reaction of alkene isomerization on $Fe(CO)_4$, is used for calculation. Therefore, for path D (aldehyde) and path K (ketone) a wide range of wavenumbers including the following three ranges of the C−H stretching vibration: (i) characteristic for the CH_2 symmetric mode, (ii) characteristic for the CRH mode and (iii) the range covering (i) and (ii) and the interval between them, were taken for the IOM calculations.

On the other hand, the hydrogen transfer should not occur when there is high electron density on the metal. If hydrogen transfer does not take place, reactions towards oxirane or carbonate can occur. It was assumed that the choice between oxirane and carbonate formation is determined by reactivity impulse of carbon dioxide. If CO_2 molecule is linear and symmetric, the oxirane is formed and carbon dioxide goes away. If CO_2 molecule is nonlinear and asymmetric, the cyclic carbonate is formed. In the IOM calculation, both ranges for free and coordinated CO_2 were used.

In IOM modeling [94] only 13 modes were taken into account, namely the three stretching modes: the M−O; the M−L and M−X (X = halogen) in metal complex, the four modes: the C−C; the C−R and the C−H stretching and C−H bending in the $RHC=CH_2$, the three mode in the CO_2 moiety and the three intermolecular modes: the M-olefin; the C−O−C asymmetric stretching in oxirane like moiety and the $H_2CRHC−OCO$ stretching mode (see Fig. 8). Eight combinations of the phases were taken into account.

For the 84 tested cases (resulting from number of the phase combinations (8), the three ranges and four products and reduced from 96 to 84 due to identical equations for particular situations for oxirane) synchronisation conditions were fulfilled in 40 cases (Fig. 9). From among 34 solutions for aldehyde, ketone and carbonate, 22 were obtained for the mechanism starting from the attack of olefin on peroxocarbonate system (combination (KR)) and 12 for other ways (see Fig. 8). Only four possible synchronisations for aldehyde, 12 for carbonate and 18 for ketone were obtained. The lowest influence of changes of the phases combination and of the ranges seems to be for the ketone formation. Only for the combination KR(RK) and KK(RK) conditions for the synchronisation were found to be not possible. It means that starting from the II or III ways (i.e., for the (RK) phase combination) in the situation when the bond Me−L is during contraction, formation of ketone is rather less probable.

Formation of carbonate is preferred when the vibrations of the Me−L and metal–halogen bonds are in the same phase: RR(□ □) or KK(□ □), where □ denotes either R or K. It would suggest that symmetry of peroxocarbonate complex can favour carbonate formation.

Formation of aldehyde is possible only on the way starting from attack of olefin on peroxocarbonate system (□ □ (KR)) combinations). Unexpectedly, synchronisation is not possible for the range characteristic for the CH_2 mode. It can suggest that formation of aldehyde runs via the assumed mechanism like 1,3-suprafacial-hydrogen shift [93] and that this step of the reaction is the determining one.

Formation of oxirane is possible on all considered ways (see Fig. 8). In full analogy to the formation of carbonate, the symmetry of peroxocarbonate complex prefers formation of oxirane. From the point of view of design of high selective catalyst for synthesis of carbonates, the last obtained result is disadvantageous.

The IOM modeling [94] supports experimental facts [83] of the low yield of organic carbon-
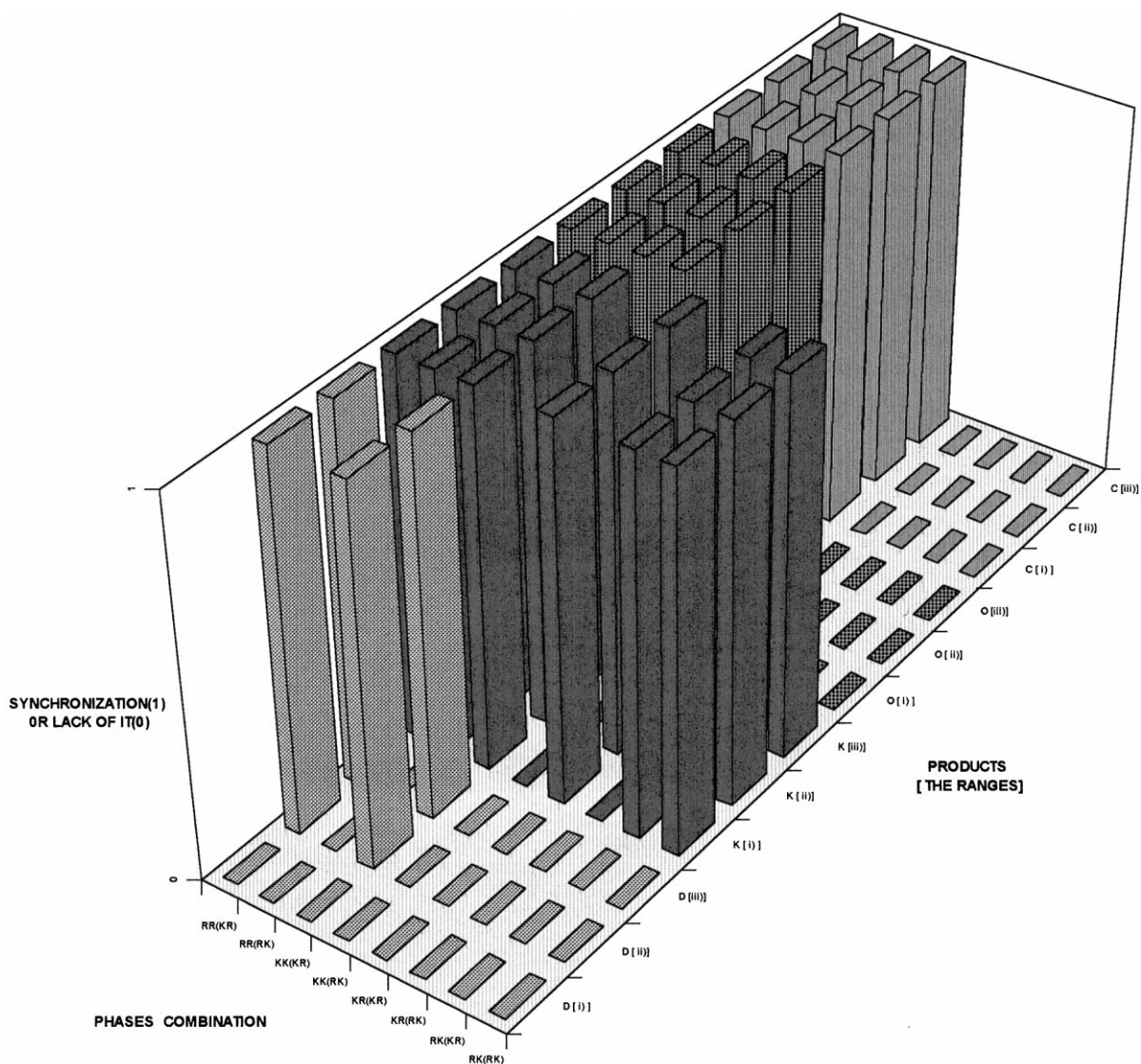
Fig. 9. An example of results of the IOM calculation for the reacting system for cyclic carbonates formation in catalytic reaction between olefins, O_2, CO_2. Scanning of possibilities of the synchronisation for the reactions of aldehyde (D), ketone (K), oxirane (O) and carbonate (C) formation, depend on the phases combination (see text) and the assumed three ranges of the C−H stretching vibration of olefin: (i) characteristic for the CH_2 symmetric mode, (ii) characteristic for the CRH mode and (iii) the range covering (i) and (ii) and the interval between them, taken for the IOM calculations.

ate using Rh-hexacoordinated species as the active catalysts. In order to find reasons of such facts, detailed analysis of vibrational ranges for synchronisation for carbonate formation reaction was performed. The results of the analysis are presented in Table 2. Most of the ranges, within the synchronisation of reactivity impulses for the reaction of carbonate formation is

possible, are identical to ranges necessary for the reaction of oxirane formation. In addition, the time of synchronisation for oxirane formation is shorter than that for carbonate formation.

The results of the application of the IOM to the complete set of reactions occurring in the system of six-coordinated peroxocarbonates $L_n XMeOOC(O)O\eta^2–O_2$ complex with olefins

Table 2
Analysis of vibrational ranges where the synchronisation for carbonate formation is possible

Vibrator	Range used for calculation [cm^{-1}]	The synchronisation subranges [cm^{-1}]
$\nu 1$	401–999	only 408–488; (common with oxirane)
	401–599	only 408–455; (common with oxirane)
$\nu 2$	370–399	377–376 and 390–392; (common with oxirane)
	201–450	201–230; 250–290; 310–330; 350–365; 390–405; 425–435; (common with oxirane)
$\nu 3$	285–330	288–287; 309–308; (slightly lower wavenumbers in comparison to these for oxirane)
	201–399	201–215; 245–250; 265–270; 325–330; 345–355; (common with oxirane)
$\nu 4$	101–199	124–123 (separated from oxirane about 30 cm^{-1}); 165–164; (common with oxirane)
$\nu 5$	1630–1699	1683–1680; 1672–1666; 1649–1642; 1693–1687; 1654–1650; (common with oxirane)
$\nu 6$	1150–1199	1150–1154; 1190–1195; 1152–1158; (common with oxirane)
$\nu 7$	1230–1270	1257–1252 (separated from oxirane about 15 cm^{-1}); 1254–1249 (separated from oxirane about 20 cm^{-1}); 1263–1260 (slightly separated); 1258–1253; (separated from oxirane about 10 cm^{-1}); 1261–1258 and 1251–1248; (separated a few cm^{-1} from oxirane)
$\nu 8$	1150–1199	1195–1191; 1154–1152; (common with oxirane)
$\nu 9$	3010–3095	3053–3066; (partly overlapping with oxirane); 3080–3092; (common with oxirane)
	3075–3095	3081–3095; (common with oxirane)
	3010–3040	3040–3029; 3037–3034; 3030–3029; 3018–3011; (common with oxirane)
$\nu 10$	820–1499	830–836; 840–842; 862–866; 912–916; 928–931; 944–946; 1016–1019; 1028–1030; 1071–1075; 1108–1114; 1190–1198; 1223–1234; 1273–1278; 1282–1285; 1298–1290; (separated); 1299–1314; 1355–1360; 1371–1374; (partly overlapping with oxirane); 1388–1394; 1437–1443; 1460–1463; 1467–1473; (common with oxirane)
	620–1430	630–650; 680–720; 780–800; 840–900; 920–980; 1000–1040; 1090–1120; 1150—1290; 1340–1440; (common with oxirane)
$\nu 11$	1240–1395	1240–1241; 1269–1274; 1314–1319; 1327–1330; 1348–1354; (common with oxirane)
	1090–1299	1115–1125; 1150–1160; 1190–1200; 1227–1240; 1263–1275; (common with oxirane)
$\nu 12$	2310–2350	2320–2338; (common with oxirane); 2340–2350; (separated)
	1650–1999	1670–1690; 1720–1750; 1765–1775; 1845–1855; 1875–1885; 1895–1910; 1983–1985; (slightly separated)
$\nu 13$	630–800	636–639; 654–657; 677–680; (common with oxirane); 649–653; 684–689; 720–731; 760–766; 773–776; (separated); 639–641; 680–682; 788–789; (separated)

RCHCH$_2$ show the low yield of formation of carbonates and aldehydes. The latter result does not agree with experiment and can be explained assuming secondary reaction of isomerization of oxirane, which predicted yield is to high. More detail presentation of the modeling one can find in the preparing paper [94].

In order to look for complexes more selective to carbonate it is necessary to change ranges used for calculation. It means that geometry, coordinate number for different metals complexes should be changed.

The IOM modeling for the five-coordinated complexes has been made [95], in full analogy to the six-coordinated complexes. The results of calculation show possibility to increase of the selectivity toward carbonate. The averaged selectivity of 23.5%, while depending on the case

considered the selectivity changes from 20% to 25%. Moreover, if one can change the phosphate ligands to nitrogen derivatives ones and chlorine to bromine ligand the selectivity can rise to 27–31%. Using both the phosphate and the nitrogen-derivatives ligands, but not the bromine ligand it was found [83] experimentally that for the five-coordinated rhodium complexes the selectivity toward carbonate changed from 20.5% to 30%.

The IOM calculations were made for the assumed wide range 400–1000 cm^{-1} for the M−O stretching mode but for the assumed relatively short time (the number $n = 1–5$ of consecutive vibrations of the M−O mode) of the synchronisation. The latter assumption means that very active catalyst had been looked for. While for ketone, the synchronisation condi-

tions were fulfilled in the following subranges: 400–550 cm^{-1}, 580–600 cm^{-1}, 630–680 cm^{-1}, 720–740 cm^{-1} and 835–850 cm^{-1}) only in low wavenumbers ranges the synchronisations were possible for the aldehyde (400–480 cm^{-1}) and for both oxirane and carbonate (400–530 cm^{-1}). Taking into account the limit of the n number of consecutive vibrations of the M–O and the vibrational periods one can conclude that in the range of higher wavenumbers (i.e., the limited shorter time for the synchronisation) just because of the limit synchronisation condition for carbonate were not fulfilled, and only very fast synchronisations for ketone were possible. In order to check such possibility the IOM calculations were repeated for the same limit time for the synchronisation. The range 400–1000 cm^{-1} for the M–O stretching mode was divided into subranges, for which different the n numbers were used. Averaged over the subrange selectivity toward carbonate was calculated. The selectivities, namely for the subrange 500–600 cm^{-1} ($n = 6$) 23.3%, for the subrange 600–800 cm^{-1} ($n = 6$–8) 24.8% and for the subrange 800–1000 cm^{-1} ($n = 6$–10) 21.9%, were the same in values as the previously calculated (the average for all subranges selectivity was 23.3% in comparison to that of 23.5% calculated for the 400–1000 cm^{-1} range). From the point of view of the IOM approach, it seems that only in the subrange 400–530 cm^{-1} of the M–O stretching mode vibration one can find catalytic system for carbonate formation.

The more detailed analysis of the results of the IOM calculation predicts, for a particular narrow subrange of frequencies of the metal–oxygen stretching mode and a particular narrow subrange of frequencies of the C–R stretching mode, possibility to obtain very high selective catalytic system for the carbonate formation. If the theoretical prediction will be of importance in practice depends on the results of our recent additional studies, which have been developed.

Auxiliary quantum chemistry calculations have been performed [96,97] for the reaction system. The complexity of the system caused, which in practice only the semiempirical PM3(tm) method, parametrized for several transition metals [98–100], could be used for the investigations of optimised molecular structures of the reacting molecules and their complexes, as well as of possible reaction paths in present of the six-coordinated or the five-coordinated rhodium catalysts. In the latter investigations, the intramolecular rearrangements were performed by a stepwise coordinate driving leading to the reaction products. After each step, the single point energy, the energy for optimised structure after removing the constraints were calculated. All minimum energy and transition state structures were verified by frequencies calculations. In all cases, only one imaginary frequency was found for the transition states and none for the stable structures. In most of the calculations, simplified models (PH$_3$ instead of phosphane ligands) of the rhodium complexes, excluding the case when for five-coordinated rhodium complex diphos (PH$_2$CH$_2$ CH$_2$ PH$_2$) were used. As the model of HRC=CH$_2$, the propene molecule was usually used, but also the styrene in a number of calculations was studied.

The computer simulations of the intramolecular rearrangement leading to the desired reaction products indicate the possibility of following qualitatively the reaction path at the semiempirical level of theory. Quantitative comparison of different reaction paths, when reaction mechanism is not known enough, have to be made with caution due to only approximate energy barriers obtained by the PM3(tm) method. Nevertheless, it seems that formation of the oxirane is preferred (for both the propene and the styrene) for different orientations of the reacting molecules and with the lowest activation energy. Only for styrene, weakly coordinated to the rhodium complex through an aromatic system, seems to be possible is the formation of the styrene carbonates. One may find an agreement between the IOM modeling results (''overproduction'' of oxirane) and this conclusion from the PM3(tm) studies. It was also shown that in the case of the five-coordinated

$(PH_3)_2RhCl$ (CO_4) model complex, an open axial position in the coordination sphere enables the olefin to approach and directly coordinate to the complex. In the next step, the two coordinated ligands (olefin and peroxocarbonate moiety) can react to form further products. Since the calculated stabilisation energy for olefin coordination is higher than the coordination of solvent molecules (benzene, THF, acetone, MeOH and water were considered), the process of solvent exchange and reaction with olefin under experimental conditions seems to be probable. These conclusions seems to be useful for an explanation of experimental evidences [83,84] supported by the IOM calculations, why the five-coordinated complexes are more efficient catalysts for the desired reaction than the six-coordinated ones. In particular, it was found [97] that in the five-coordinated rhodium complex with the diphos ligand, the reaction of carbonate has the lowest energy barrier in comparison to model complexes with the PH_3 as the ligand.

5. Future development

The aim of the presented studies was to show that simple Impulse Oscillation Model (IOM) can serve as a practical tool for design of catalytic molecular devices for a desired reaction. It was shown that for the simplest catalytic systems like the trimolecular system of two molecules of amines and one molecule of carbon dioxide — where ab initio quantum chemistry methods can be used — the prediction of the IOM is in good agreement with the results of more time consuming calculations based on these classical methods. Moreover, in the cases of more complex systems where use of these methods is not possible, the IOM is still useful. Despite of the permanent improvements of the IOM softwares developed by Jamroz [101], in order to make the tool more and more user friendly, the softwares for computer-aided design of real catalyst seems to be still a long-term

goal. In such future softwares, an engineer, delivering known information on a desired thermodynamically possible reaction (reactants, products, possible mechanisms) as input data, should obtain as output data a set of recommended promising molecular catalysts.

At least the following three problems have to be solved to achieve this long term-goal:

- translation of the obtained with IOM sets of vibrational ranges for considered modes in a catalyst into sets of catalyst vibrators with known chemical compositions;
- dependence of averaged activity and selectivity of large population of designed molecular catalysts on their distribution in the population
- practical aspects of organisation at macroscopic level of the necessary direct energy flows at molecular level.

The first problem seems to be the most difficult one. Recently, it has been proven [102] that from the prediction of the IOM sets of wavenumber ranges, using the theoretical spectroscopy methods, one can obtain a finite set of vibrators. We have [103] looked for a procedure using the shifts of the frequencies, resulting from comparison of the calculated with the IOM model frequencies and ones for non-interacting reactant and catalytic centre, as the base data instead of the real systems for ab initio quantum chemistry calculation. The simplest example of such approach can be the use of well known shifts of a metal–ligand stretching mode frequency depending on geometry of metal complex used as a homogeneous catalyst. More systematic experimental and theoretical studies about the strong solvent effect, from the point of view of the approach presented in this paper, should be developed.

Until now the simplest practical way seems to be the use of experimental spectroscopy databases, as well as, to make auxiliary quantum chemistry calculations for simplify poten-

tial catalytic systems for which the experimental data are not available. We have studied in this way systematically the reacting systems that are in our field of interest. One can expect that the use of combinatorially synthesised libraries [104,105] combine with the predicted with IOM ranges of frequencies of vibrators of potential catalysts will be useful in practice. Interdisciplinary approach, in particular, surface science and material science in the case of heterogeneous catalysts should be helpful.

It seems that classical methods of the heterogeneous catalysts preparation like precipitation, impregnation, etc., will be of less importance in the future synthesis of designed catalysts. Nanotechnology [106] seems to be ready as a tool of preparation of tailor-made heterogeneous catalysts. From the point of view of the system approach, presented in this paper, such catalysts should be treated as a set of catalytic molecular devices. Design of such catalyst means, in fact the design of not only the device but also the population of the devices. Usually, in present state of art of synthesis of heterogeneous catalysts, only a small part of surface sites serve as catalytic active sites [107]. The systematic study on the design of the properties of the devices populations, differ in distributions of slightly different devices, has been started [103]. In the case of homogeneous catalysts, one may expect that the well known strong solvent effect can be, at least partially, connected with the shifts of frequencies of catalyst modes. There is need for systematic experimental spectroscopy studies in this field.

The problem of practical aspects of organisation at macroscopic level of the necessary direct energy flows in catalytic molecular devices seems to be the one of key factor determining averaged activity, selectivity and life time of real industrial catalysts. The problem was discussed in this paper from the point of view of the proposed system approach. In the above described models of multicatalytic system, it was shown that one of the possible effective way to solve this problem can be the energy

coupling between a few number of catalytic devices each of which realising one step of a multistep reaction. Such solution seems to be used in multienzyme systems. To design such organisation one has to take into account the well-defined energy and time requirements [36]. Therefore, such possibility should be useful in the cases when one will design catalytic systems mimicking multienzyme system rather than a particular desired reaction.

Efforts have been made [51] to find a basis for the SET and IOM models generalisation. A common physical picture of the catalytic act combining together the activation energy transfer and the synchronisation as a consecutive sequence of events were suggested. It is expected that such approach combined with study on necessary energy flow from activated center and from product molecule, which have been developed [103], will result in practical rules of the organisation of energy flow at macroscopic level. Notice that in the case of use of nanotechnology, one must additionally take into account quite different quasiparticles of elementary excitation (e.g., plasmone and magnone) as possible carriers of discrete energy flows inside nanostructures, in comparison to the quasiparticles of typical solids have been used as modern catalyst.

In order to avoid misunderstanding, it must be pointed out that the above presented considerations based on the assumption that macroscopic activity and selectivity of a design and next synthesised catalyst depend only on a distribution of molecular level activities and selectivities in the population of its active sites. It should be true in the proposed approach to design of new catalyst, if one has looked for the best catalyst for a desired reaction. On the other hand, it is well known that selectivity and activity of heterogeneous industrial catalysts depends on many factors including the transport of mass and heat both inside a pellet, a sphere or other forms, and in the whole catalytic reactor, possible consecutive reactions, etc. In particular, well known from many years the shape selectivity of

zeolites determines their selectivities toward desired products in many petrochemical processes. Combining the collected knowledge and experience in industrial catalysis with the proposed system approach to design new catalyst, can help to achieve the progress in the way toward the long-term goal of computer-aided design of real catalyst.

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