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Catalysis and non-equilibrium thermodynamics: modern in situ studies and new theoretical approaches

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Abstract

The paper discusses some modern approaches which consider the state of operating catalysts from the point of view of non-equilibrium thermodynamics. Both theoretical speculations as well as experimental data of some in situ studies are considered. An emphasis is put on the *stable* non-equilibrium states of catalysts. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last two decades we have seen a number of breakthroughs in the detailed understanding of the catalyst action in many model or practically important catalytic systems, both homogeneous and heterogeneous (see, e.g., recent reviews [1–4]). However, most of such studies were deeply mechanistic and restrict themselves to finding the most probable intermediates of the catalytic reactions as well as the relevant kinetic schemes of the surface or bulk reactions leading to the catalytic phenomena. For this reason, despite significant achievements in a physico-chemical modelling of particular catalytic systems following from the above considerations, these results can only be applied typically to the very particular reactions only and thus, as a rule, give only a moderate success in attempts to generalize the understanding of the catalysis as a very specific but nevertheless general physico-chemical phenomenon.

Creation of a suitable general physico-chemical background for heterogeneous catalysis was a field of very serious attention of Academician G.K. Boreskov, thermodynamics having been recognized by him as one of the most important cornerstones. A top issue of this recognition seems to be the well known and widely experimentally confirmed “Boreskov's rule” on an approximate constancy of the specific catalytic activity: “Upon the interaction of a catalyst with the reaction medium, the resulting stationary specific activity of the heterogeneous catalysts of the same chemical composition and under the same reaction conditions should be approximately equal, if the catalyst maintains its phase composition” [5,6]. This rule is based on the thermodynamic considerations and results from the expectation of the adjustment of the composition and therewith the properties of the catalyst surface to external conditions imposed

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by the reaction medium, thus demanding a certain reconstruction of the catalyst surface as a general issue for catalysis.

There are also a few other well-known general thermodynamic statements to be taken into account when considering catalytic phenomena. First of all, it is clear that a *catalyst cannot shift a thermodynamic equilibrium* between the reactants and products of the catalysed reaction. Another statement is expressed by the so-called "Horiuti–Boreskov's relationships" [6,7]. These relationships show that the overall rate of a reversible catalytic reaction is determined by the difference of the rates between the forward and backward directions and increases with the deviation of the reaction mixture from its thermodynamic equilibrium. Also, well known are various correlations between the rate of catalytic reactions and the energies of intermediate chemical interactions of the catalyst with the reactants (and products).

However, there is a very serious obstacle for immediate implementation of conventional "equilibrium" thermodynamics to describe the state and behaviour of *operating* catalysts. Indeed, it is easy to see that catalysis is principally a *non-equilibrium* phenomenon. A principal point of this non-equilibricity is that all the chemical transformations as well as the other physico-chemical phenomena occurring with a catalyst in the course of its operation have to be considered as *being coupled with the main "coupling" reaction*. The latter is evidently the reaction to be catalysed. Thus, the main driving force of all chemical transformations of the catalyst that controls its state, and consequently, its catalytic properties, is the De Donder affinity A of this latter coupling reaction (or, in other words, the change of Gibbs energy $\Delta_r G$ in the catalysed reaction). This statement is very easy to demonstrate even when considering the catalysis of a simple reaction such as

$$A \rightleftarrows B$$

Driven from the left to the right, the affinity of this reaction is $A \equiv -\Delta_r G > 0$. In the case that the mechanism of this catalytic transformations is described by a simple scheme

$$A + K \rightleftarrows AK, \quad AK \rightleftarrows B + K, \tag{1}$$

where K is a "free state" of the catalyst active site, while AK is an intermediate complex of this site with the reactants, and the above transformations may be represented by a closed loop diagram:

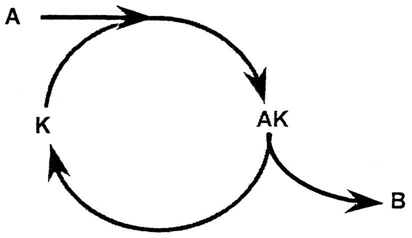

Fig. 1 is the corresponding energy diagram of the above transformations in terms of chemical potentials μ of the reagents, the catalyst free site, and the intermediate complex. It is evident that in order for the overall reaction to be able to proceed from the left to the right, the current chemical potential μ_{AK} of the intermediate complex has to be located *between* the chemical potentials of the starting and final groups of reactants, namely between $(\mu_A+\mu_K)$ and $(\mu_B+\mu_K)$. This means that the actual chemical potential of the intermediate complex *is dependent* on those of the reactants and thus the intermediate chemical interactions of reactants with the catalyst are indeed those processes coupled with the main catalysed process. Thus, in the course of any catalytic reaction, the catalyst unavoidably exists in a *thermodynamically non-equilibrium state* (either stationary or of another kind). Evidently, this state is determined by "thermodynamic forces" acting in the non-equilibrium system. Over the last decade, a lot has been done in order

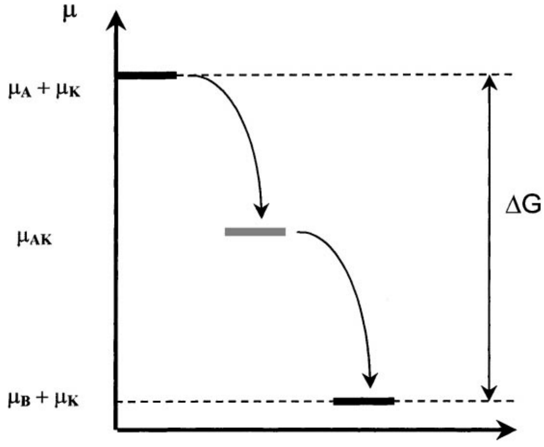

Fig. 1. Free energy diagram of catalytic transformations according to scheme (1).

to approach non-equilibrium thermodynamics to consider the behaviour of catalysts. The aim of this paper is to summarize some of the recent ideas generated in this area.

2. Recent in situ studies of catalysis and non-equilibrium thermodynamics

Usually, to consider the state of an operating catalyst and details of its behaviour, a *direct kinetic* approach is utilized. This approach consists of writing down and solving a particular set of differential kinetic equations. The evident advantages of "pure" kinetic approach to describe the thermodynamically non-equilibrium processes in the reacting chemical systems are the well-elaborated methods to represent kinetic equations and of their solutions, the well-elaborated criteria of stability of kinetic systems, as well as the possibility of describing very particular dynamic events in catalysis such as different kinds of oscillations, "limiting cycles", bifurcations, bistabilities, chaotic modes, etc. Evidently, implementation of the direct kinetic approach involves simultaneously an a priori statement or knowledge of a particular scheme of chemical transformations as well as an attribution of respective rate constants to all the elementary (or effective) reactions.

Unfortunately, this approach is not very fruitful for making generalizations of the analyses. Indeed, the direct chemical kinetic approach looks like classical mechanics, allowing one to forecast the strict destination of a dynamic system only if the exact starting (initial) conditions and the concrete dynamic equations of the time evolution of the system are known. On the other hand, for complicated kinetic schemes, one should expect an unpredictable or large dependence of the final results on the choice of particular set of reactions and/or reaction schemes and on assumptions of the reversibility of the reactions. This creates an evident disadvantage of the direct kinetic approach: the "pure" kinetic analysis appears to be too abstract or have no "physical clarity". To remove this disadvantage, one should introduce "*driving forces*" of process under kinetic consideration; otherwise there are few possibilities of making any generalizations of the results of the analysis. Furthermore a "pure" kinetic approach gives no possibility of describing the typical "thermodynamics relevant" phenomena such as displacements of phase equilibria, etc.

From a mechanical point of view, it is possible to make generalizations in the analysis by moving to the statistical physics. Similarly, for the analysis of chemical transformations, the role of statistical physics is played by thermodynamics which gives a more suitable language for the generalization of possible conclusions on the direction of the dynamic evolution of complex chemical phenomena by emphasizing the main *driving forces* of the evolution even despite little knowledge on the real internal mechanism of the process.

Non-equilibrium dynamic phenomena is the field of non-equilibrium (irreversible) thermodynamics, a subject which has been developed since the middle of this century. Unfortunately, direct application of the most elaborate *"linear" non-equilibrium thermodynamics* [8] to describe real catalytic phenomena is not possible. Indeed, "linear" thermodynamics deals only with the dynamic systems which are close to their thermodynamic equilibrium. For a chemical reaction, this means that the rate, v, should be proportional to the thermodynamic driving force, i.e. to the current value of the affinity A of the reaction. It is well known (see, e.g., [8,9]) that for temperatures in the range 300–1000 K, this follows in severe restrictions for the allowed values of chemical affinity A: $|A| < RT \approx 2\text{–}6\,\mathrm{kJ/mol}$ (R is the universal gas constant, T is the temperature). Note, however, that for all real catalytic processes (generally, even for many kinds of the isotope exchange reactions), $|A| > RT$. Thus, *real catalytic systems are usually far from equilibrium*, and therefore, far from the "linear" region.

For example, Prigogine's theorem on the direction of the evolution of a dynamic system states: "When being close to a thermodynamic equilibrium, the system experiences an evolution toward a stable stationary state characterized by a minimum of the entropy production rate". This means that the value of

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{(\text{rate of chemical reaction}) \cdot (\text{its affinity})}{T}$$

should tend under the above conditions to a minimum. However, the direct application of this very important issue to catalysis is seriously restricted, since catalytic systems do not obey the conditions of linear non-equilibrium thermodynamics.

This operation of real catalysts occurs *everywhere under conditions of "non-linear" non-equilibrium thermodynamics*. This complicates the consideration of various phenomena and focuses the attention of the researchers on finding phenomena, expected solely for non-linear non-equilibrium thermodynamics. Among such phenomena is the creation of so-called "temporal (or spacio-temporal) dissipative structures" which are attributed to the existence of a *non-stable state* of the system and are easily recognized due to their specific behaviour.

Over the last two decades, numerous in situ studies have been performed over heterogeneous catalytic processes which have provided evidence for "non-linear non-equilibrium" behaviour of some catalysts during their operation. For example, direct in situ studies of heterogeneous catalysts have given evidence for the existence of a large variety of peculiar "non-linear" phenomena such as isothermal oscillations of the rates of catalytic reactions as well as propagation of chemical waves on a catalyst surface on mesoscopic and even atomic scales [4,10–13]. Both phenomena originate from the possibility of instabilities in the steady state of an operating catalyst. Note that the appearance of isothermal oscillations in the rates of catalytic processes, as well as the creation of spacio-temporal patterns, are observed for both homogeneous (a well-known example since 1956 is the "BZ" reactions) and heterogeneous systems. These are generally attributed to "strong" non-linearities of the catalytic processes.

In contrast, until now much less is known of "non-linear" (in the above sense) non-equilibrium phenomena related to the *stable steady state* of operating catalysts. This state seems to be the most common for "regular" catalysis. Thus, understanding of these phenomena is of the highest priorities for the general practice of catalysis. Note that such "stable" phenomena lead, for example, to the reconstruction of the catalyst surface as well as to a change in the catalyst phase equilibrium under the action of the reaction medium, this being responsible for validity of the "Boreskov's rule".

This paper draws attention to a few phenomena of general importance which can result from the thermodynamic non-equilibrium nature of the stable state of the operating catalyst.

3. Introducing the chemical potential in describing the state of operating catalysts

As usual, the principal parameter for considering operating catalysts from the thermodynamic viewpoint should be the *chemical potential*, μ, of the catalyst reaction sites and of the reaction intermediates. Note that we have to consider these parameters *under operation conditions* rather than in equilibrium. According to our recent experience, the most suitable language for this appears to be a joint kinetic–thermodynamic analysis of chemical processes which allows one to discuss any chemical kinetic phenomena in terms of chemical potentials of the reagents involved rather than in terms of their concentrations [14]. A way to introduce the notion of chemical potential into the analysis of dynamic chemical phenomena is very simple and results from a "thermodynamic" form of kinetic equations.

Traditionally, the rate v_{ij} of an elementary chemical reaction (which should unavoidably be reversible due to the principle of detailed balance) between two groups or reagents i and j is expressed as

$$v_{ij} = k_{ij}\prod_{\alpha} C_{\alpha}^{\nu_{i\alpha}} - k_{ji}\prod_{\alpha} C_{\alpha}^{\nu_{j\alpha}}. \tag{2}$$

Here the parameters are: the rate constants $k_{ij} = (k_{\mathrm{B}}T/h)\exp(-\Delta G_{ij}^{0\neq}/RT)$ of the transformation of reactant group i into the group j, the concentration C_{α} (α=1, …) of substance α involved; the stoichiometric coefficients, $\nu_{i\alpha}$; $\Delta G_{ij}^{0\neq} = G_{ij}^{0\neq} - G_{i}^{0}$ is the standard Gibbs energy for activation in the reaction, while $G_{ij}^{0\neq}$ and G_{i}^{0} are the standard Gibbs energies of formation of the transient state and the reactant group i, respectively. Note that $G_{i}^{0} \equiv \mu_{i}^{0}$ and $k_{ij} \neq k_{ji}$ for $\Delta G_{ij}^{0\neq} \neq 0$.

Since for systems close to ideal, one can write $\mu_{\alpha} = \mu_{\alpha}^{0} + RT\ln C_{\alpha}$, it is possible to rewrite (2) as

$$v_{ij} = \epsilon_{ij}\{\exp(\mu_i/RT) - \exp(\mu_j/RT)\} \equiv \epsilon_{ij}\{\tilde{n}_i - \tilde{n}_j\},$$

where

$$\tilde{n}_i \equiv \exp(\mu_i/RT) \equiv \exp\left(\sum_{\alpha} \nu_{i\alpha}\mu_{\alpha}/RT\right) \equiv \prod_{\alpha} \exp(\nu_{i\alpha}\mu_{\alpha}/RT) \equiv \prod_{\alpha} \tilde{n}_{\alpha}^{\nu_{i\alpha}}$$

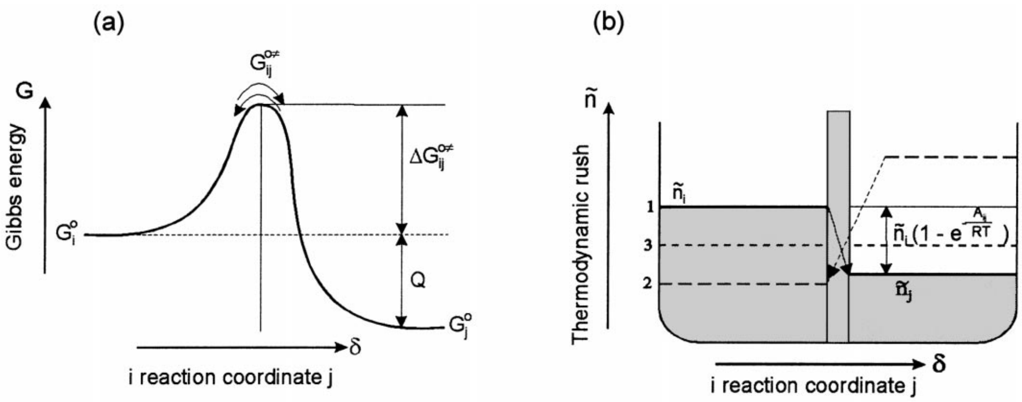

Fig. 2. Schematic representation of an elementary reaction in traditional coordinates with an activation barrier and activation energy E^0 (a) and in coordinates with "thermodynamic rushes" $\tilde{n}_i$ of the reactants (b). For the second case, the occurrence of the reaction looks like a flowing liquid between two pools separated by a membrane with permeability proportional to ϵ_{ij}; here the lines for the reaction from the left to the right as well as for the opposite direction are given (lines 1 and 2, respectively), line 3 represents the system in thermodynamic equilibrium (according to Okunev and Parmon [14]).

and

$$\epsilon_{ij} \equiv k_{ij}\exp(-\mu_i^0/RT) = \frac{k_B T}{h}\exp(-G_{ij}^{0\neq}/RT).$$

Here μ_i and μ_i^0 are the actual and standard values of the chemical potential of the reactant group i:

$$\mu_i = \sum_{\alpha} \nu_{i\alpha}\mu_{\alpha}.$$

The affinity of the reaction being equal to

$$A_{ij} = \mu_i - \mu_j.$$

Thus, in the "thermodynamic (or "canonic" [9]) form" the overall rate of an elementary reversible reaction should be expressed as

$$v_{ij} = \epsilon_{ij}\{\tilde{n}_i - \tilde{n}_j\}. \tag{3}$$

The principal parameter in this expression is $\tilde{n}_i \equiv \exp(\mu_i/RT)$ well known in thermodynamics as "absolute activity" of the reactant group i [15]. For our considerations, it also seems worthwhile to call this parameter the "thermodynamic rush" of the reactant group [14]. Note also, that if the reaction proceeds outside the "linear" region of non-equilibrium thermodynamics, its rate is *proportional* to the *difference of thermodynamic rushes* rather than being proportional to the simple affinity of the reaction. When approaching the thermodynamic equilibrium of the transformation under consideration, the dependence in the "rushes" $\tilde{n}_i$ and $\tilde{n}_j$ obviously becomes proportional to the affinity A_{ij}.

The second parameter ϵ_{ij} is a "reduced" rate constant or "permeability" of the potential barrier. Note, that in contrast to k_{ij}, ϵ_{ij} *does not depend* on the thermodynamic parameters *of the reactants* themselves, being *dependent* only on the standard parameters of the *transient state* between the reactant groups i and j. As a consequence, $\epsilon_{ij}=\epsilon_{ji}$.

Thus, according to the above approach, in the "thermodynamic" form, the overall rate v_{ij} of elementary chemical processes is expressed as a function of the actual chemical potentials $\mu_i = \sum_{\alpha} \nu_{i\alpha}\mu_{\alpha}$ of the "reactant groups" (the groups of reagents involved in the chemical transformations) rather than of their concentrations. The above approach is very useful for providing a joint kinetic–thermodynamic analysis of the chemical reaction systems and is greatly simplified for a graphical representation (see Fig. 2).

The suggested approach is known to be valid not only to the "thermodynamically ideal" systems. A general framework for the approach are the so-called Marcelin–De Donder kinetics and kinetics of the mass-action type with the detailed balance concept. Among the steps which have been taken into elaborating this approach, one should mention the "De Donder's" chemical affinity (1922–1927), the formulation of linear non-equilibrium thermodynamics by Prigogine (in 1947), and the formulation of the Horiuti–Boreskov rule by Horiuti [7] and Boreskov [5] (1945–1964). Later, the relationships between the reaction rates and of the reaction affinities [16] were discussed, as well as the axiomatic treatment of (linear) chemical reaction systems [17], the analyses of complex reaction systems via Lyapunov function [18], the thermochemistry of reacting materials [19,20], the "canonic form" of kinetic equations [9], and attempts to find general equations for the rates of stationary catalytic processes [6].

A very important advantage of the above joint kinetic–thermodynamic approach is the *separation* (in the parameters under use) of thermodynamic potentials of "real" chemical structures such as reagents or intermediates and of "virtual" structures such as transient states. Indeed, all the thermodynamic parameters of the reagents and the intermediates appear to be accommodated in the parameters $\tilde{n}_i$, while for ideal systems, the parameter ϵ_{ij} appears to be dependent only on the standard value of the thermodynamic parameters of the respective transient states in contrast to conventional rate constants. For non-ideal systems like, for example, catalyst' reaction centres with significant lateral interactions, one can expect a certain dependence of ϵ_{ij} on the surface coverage and/or composition of surface layer; however, even in such a situation formula (3) seems to remain valid.

4. Application of joint kinetic–thermodynamic approach for analysing both catalytic reactions and the non-equilibrium state of catalysts

A very important simplification for our analysis is a statement that for the stable stationary occurrence of a catalytic reaction, any reaction centre of the catalyst can be considered as if in a steady state. This must be evident, since in the course of a catalytic reaction the reaction site should perform a very large number of turnovers during its lifetime.

All the general conclusions discussed below are obtained for catalytic systems whose behaviour is linear in respect to their active centres, i.e. for catalysts with "single" isolated active centres. However, one can show that the validity of many of the conclusions can be extended to more complicated catalytic systems with stable steady states, even in the case of the existence of the mutually interacting active centres.

Some of the most interesting conclusions obtained to date via the kinetic–thermodynamic analysis are presented below.

4.1. Criteria of kinetic irreversibility of chemical reactions

The joint kinetic–thermodynamic analysis allows one to obtain the correct thermodynamic criteria for the notion "kinetic irreversibility" of particular stages in any set of reactions, including the catalytic reactions, in a straightforward way. These criteria are equivalent to the statement that the rate of any backward elementary reaction is negligible in comparison to the rate of the forward reaction. From expression (3), it is evident that this corresponds to the situation where $\tilde{n}_i \gg \tilde{n}_j$. Thus, for kinetic irreversibility of a particular stage in a consecutive chain of chemical transformations, the correct criterion for irreversibility should be a significant decrease of the actual values of the chemical potentials of the respective consecutive intermediates; it is evident that it should exceed the value of *RT*.

For example, if we consider conditions of kinetic irreversibility for a catalytic transformation of R into P through consequent reactions such as

$$\mathrm{R}+\mathrm{K} \overset{\epsilon_{0,1}}{\rightleftarrows} \mathrm{X}_1 \overset{\epsilon_{0,2}}{\rightleftarrows} \cdots \rightleftarrows \mathrm{X}_n \overset{\epsilon_{n,n+1}}{\rightleftarrows} \mathrm{K}+\mathrm{P},$$

with a set of intermediates, X_i, we should take into account that for any kinetically irreversible step *i* of consecutive reactions

$$\tilde{n}_i \gg \tilde{n}_{i+1}, \quad \text{or} \quad \exp(\mu_i/RT) \gg \exp(\mu_{i+1}/RT),$$
$$\text{or} \quad \mathrm{A}_{1,i+1} = \mu_i - \mu_{i+1} > RT.$$

Here μ_i is the chemical potential of the complex of the reaction intermediate X_i with the active site of the catalyst. Since, in a steady state, the overall rate of the process is given by

$$V = \epsilon_{0,1}(\tilde{n}_\mathrm{R}\tilde{n}_\mathrm{K} - \tilde{n}_1) = \epsilon_{1,2}(\tilde{n}_1 - n_2)$$
$$= \cdots = \epsilon_{n,n+1}(\tilde{n}_n - \tilde{n}_\mathrm{P}\tilde{n}_\mathrm{K}),$$

in a situation in which all the reactions are kinetically "irreversible",

$$V = \epsilon_{0,1}\tilde{n}_\mathrm{R}\tilde{n}_\mathrm{K} \approx \epsilon_{1,2}\tilde{n}_1 \approx \cdots \approx \epsilon_{n,n+1}\tilde{n}_n = \epsilon_\mathrm{eff}\tilde{n}_\mathrm{R}\tilde{n}_\mathrm{K}.$$

Thus, the limiting step in such transformations appears to be the first one. This conclusion is well known and can be derived via a direct kinetic analysis, but in a much more complicated fashion.

A new and very important conclusion from the above considerations is that for a sequence of chemical reactions with total affinity A, the *maximum number of kinetically irreversible steps is restricted by the value of A/RT and cannot exceed this value*. Note that we cannot easily obtain this very simple restriction through direct kinetic analysis. It is never applied in the construction of complicated schemes for catalytic reactions.

The joint kinetic–thermodynamics analysis of consecutive reactions also allows one to specify more definitely the term "rate limiting step": this is a step with the largest fall in thermodynamic rush (or chemical potential) of the intermediates (see Fig. 3).

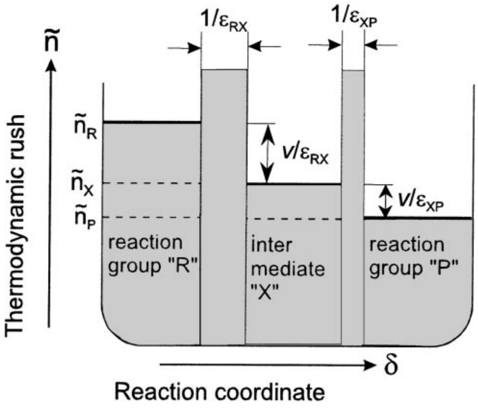

Fig. 3. Definition of the rate limiting step for the reaction $R \rightleftarrows X \rightleftarrows P$ occurring with the steady-state rate v. In this diagram this is the first step with the higher drop in thermodynamic rushes (according to Okunev and Parmon [14]).

4.2. Steady-state rate of simple catalytic reactions

It is easy to show that for not too complicated catalytic reactions occurring in the steady state, the overall rate of the process is *proportional to a difference in "thermodynamic rushes"* of the initial reaction group (or reagent) and the final reaction group (or product). Thus, this difference can be considered as the driving force for the evolution of the system and therewith will linearize the equations for the fluxes of the thermodynamic parameters. This situation is principally advantageous for providing a thermodynamic analysis since, from the beginning, it allows one to make an easy analysis of many systems *belonging to the "non-linear" region* (from the point of view of the relation between the rate and the reaction affinities) *of irreversible thermodynamics*. It therefore allows one to operate in a simple manner away from the neighbourhood of the thermodynamic equilibrium, where a linearization with respect to thermodynamic forces results from proportionality to v_{ij} to the reaction affinity $A_{ij} \equiv \mu_i - \mu_j$.

The above statement is very easy to verify by considering an analogy between the mathematical expressions describing the occurrence of an arbitrary set of monomolecular (or reduced to them [14]) reactions and those for an electrical circuit with active resistors (see Fig. 4 and [21]). Indeed, while the rate v_{ij} of an elementary reaction ij is expressed via relation (3), the current I_{ij} passing through a particular

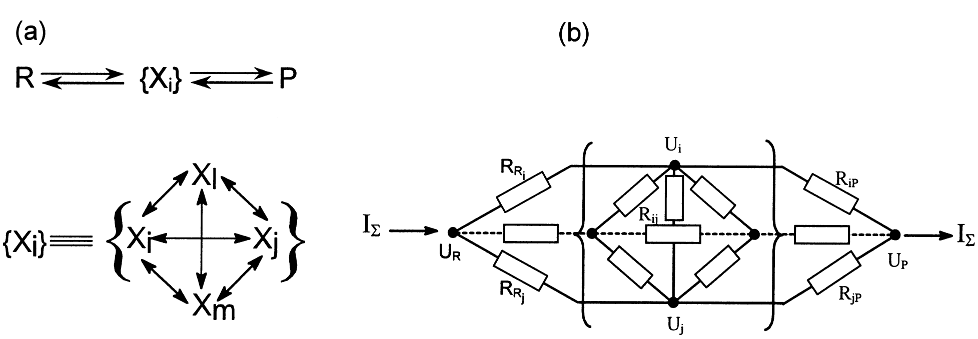

Fig. 4. The analogy between an arbitrary set of monomolecular chemical reactions (a) and an electrical circuit with active resistors (b). R and P are the initial reagent and the product, respectively, while U_R and U_P are electric potentials of the ends of the electric circuit.

"active" resistor R_{ij} may be expressed as

$$I_{ij} = \frac{U_i - U_j}{R_{ij}} \equiv \sigma_{ij}(U_i - U_j),$$

where U_i is the electric potential at point i.

Thus, since the total current $I_{\sum}$ through the circuit is

$$I_{\sum} = \sigma_{\text{eff}}(U_{\text{R}} - U_{\text{P}}),$$

where σ_{eff} is an algebraic combination of the elementary values σ_{ij}, the overall rate $V_{\sum}$ of the reagent-to-product transformation in the steady state (in this case, for mass balance, we follow the same conservation law as for electric current at any point i of the scheme) should also be expressed as

$$V_{\sum} = \epsilon_{\text{eff}}(\tilde{n}_{\text{R}} - \tilde{n}_{\text{P}}).$$

Here ϵ_{eff} is the effective value of the reduced rate constant calculated as an algebraic derivative of the elementary constants, ϵ_{ij}.

It is of interest that here the thermodynamic rush $\tilde{n}_i$ plays the role of the electric potential U_i at point i, while parameter ϵ_{ij} is equivalent to the electric conductivity σ_{ij}=1/R_{ij} of a particular part of the circuit. Thus, since equations of type (3) are widely valid, including conditions far from equilibrium, it is easy to find for many not too complicated catalytic systems, that their stationary rates should obviously be *proportional to the difference of "thermodynamic rushes" of the initial reagents and the final products* (see also Section 4.4). This gives directly the main Horiuti–Boreskov rule [5,6] showing the dependence of the stationary rate of most catalytic processes on their distance from thermodynamic equilibrium.

In the case that the catalytic system is close to the equilibrium, the stationary rate is evidently proportional to the affinity of the "coupling" reaction at any mechanism of the catalytic transformations.

4.3. *Kinetic potential (the Lyapunov function) for relatively uncomplicated catalytic reactions*

Construction of a kinetic potential, i.e. a Lyapunov function which is at a minimum in the steady state of the reaction scheme, is usually considered to be an extremely difficult task. However, it is easy to verify in a direct way that for an arbitrary set of monomolecular reactions, expressed in Fig. 4(a), the role of the above Lyapunov function Φ is played by a combination of terms [14]:

$$\Phi = \sum_{ij} \epsilon_{ij}(\tilde{n}_i - \tilde{n}_j)^2 + \sum_{i} \epsilon_{\text{R}i}(\tilde{n}_{\text{R}} - \tilde{n}_i)^2 + \sum_{j} \epsilon_{j\text{P}}(\tilde{n}_j - \tilde{n}_{\text{P}})^2, \tag{4}$$

or in the general case of indexing elementary reactions,

$$\Phi = \sum_{ij} \epsilon_{ij}(\tilde{n}_i - \tilde{n}_j)^2.$$

Minimization of function Φ should be performed with respect to all "dependent internal" parameters, $\tilde{n}_i$ and $\tilde{n}_j$, while $\tilde{n}_{\text{R}}$ and $\tilde{n}_{\text{P}}$ serve as the "independent external" parameters. Formula (4) is easily derived by considering the rate of entropy production in the system [8,14]. Note that the Lyapunov's function Φ for the steady state is totally similar to thermal power dissipated in the analogous electric circuit shown in Fig. 4(b).

This result corresponds well with the general statement of the main Prigogine theorem on the evolution of a dynamic system to the steady state [8]. Nevertheless, our result should be considered on a much broader scale since it is also valid for at least particular kinds of chemical systems which are far from the thermodynamic equilibrium.

The same approach can be applied to analysing the arbitrary path for the monomolecular or quasimonomolecular dynamic evolution of the complex "reagent–active centre"

$$\text{R} + \text{K} \rightleftarrows \{\text{X}_i\} \rightleftarrows \text{P} + \text{K}. \tag{5}$$

The steady state for this scheme refers to minimum of the expression

$$\Phi \equiv \sum_{i,j} \epsilon_{ij}\left(\frac{\tilde{n}_i}{\tilde{n}_{\text{K}}} - \frac{\tilde{n}_j}{\tilde{n}_{\text{K}}}\right)^2 + \sum_{i} \epsilon_{\text{R}i}\left(\tilde{n}_{\text{R}} - \frac{\tilde{n}_i}{\tilde{n}_{\text{K}}}\right)^2 + \sum_{i} \epsilon_{i\text{P}}\left(\tilde{n}_{\text{P}} - \frac{\tilde{n}_i}{\tilde{n}_{\text{K}}}\right)^2.$$

Here, the summation is made over all the possible intermediates i, j of the catalytic transformations, while $\tilde{n}_{\text{R}}$, $\tilde{n}_{\text{P}}$, and $\tilde{n}_{\text{K}}$ stand for the "thermodynamic rushes" of the initial reagent, final product, and "free" (non-occupied) state of the reaction centre. The minimization should be made by varying the values $(\tilde{n}_i/\tilde{n}_\mathrm{K})$, $(\tilde{n}_j/\tilde{n}_\mathrm{K})$ at fixed values of $\tilde{n}_\mathrm{R}$ and $\tilde{n}_\mathrm{P}$.

Hence, for any "*simple*" (i.e. undergoing only monomolecular or reduced to them [14] transformations) *reaction complex* between the catalyst active site and the reactants, the dynamic evolution to a steady state is related to the state of the catalyst with a *minimum dissipation of energy* by transformations of the complex.

An important remark from the above analysis is that the reversible dynamic evolution of the system to the real steady state of the catalyst is accompanied in many cases by a reversible reconstruction of the catalyst which seems to follow at the *minimum possible rate* of the catalytic reaction under the given conditions. The "fresh" forms of the catalyst, which were for a given process temperature, initially at thermodynamic equilibrium with the medium consisting either of an incomplete set of the reagents, or, vice versa, of an already *thermodynamically equilibrated* mixture of the reagents, seems to be more catalytically active at the start of the catalyst operation than after the arrival of the catalysts to the real steady state. The above statement on a reversible "self-inhibition" of the operating catalyst follows from the necessity to minimize the rate of entropy production in the real steady state. The validity of this demand for many catalytic systems is easily demonstrated by analysing the simple detailed schemes of the reactions with participation of catalysts capable of reversible phase transitions.

A direct consequence from the possibility of constructing the Lyapunov function Φ for a catalytic reaction scheme (5) is the obvious conclusion that the steady state of operating catalysts with the isolated reaction centres is *stable*. This conclusion appears to be valid for catalytic reactions of any complexity (including autocatalytic ones with respect to desorbing products) only if one also assumes that there is no mutual interaction between the active centres of the catalyst even though the reaction passes through short-lived intermediates in the gas (or liquid) phase. It is also possible to show, that in order for the steady state of an operating catalyst to be non-stable, one should have *at least one kinetically irreversible stage with a mutual interaction between the reaction centres*.

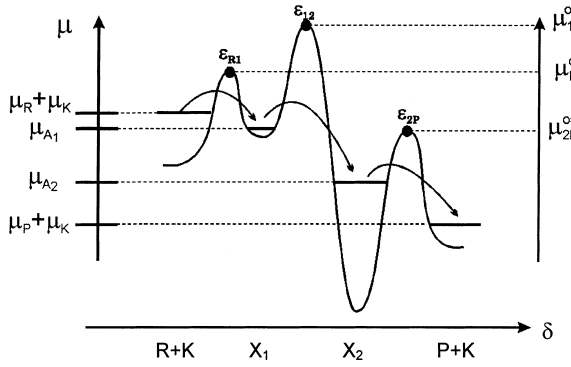

Fig. 5. The Gibbs energy or chemical potentials diagram for the steady-state occurrence of reaction $\mathrm{R+K}\rightleftarrows\mathrm{X_1}\rightleftarrows\mathrm{X_2}\rightleftarrows\mathrm{P+K}$. Note that the intermediate chemical transformations occur from the steady-state values of μ_{A1} and μ_{A2}, and their rates are dependent on the differences between the corresponding thermodynamic rushes and the values of the reduced rate constants ϵ_{ij} which are functions of standard chemical potentials $\mu_{ij}^{0\neq}$ of the transient states only.

4.4. *Independence of the steady-state catalytic reaction rate of the standard thermodynamic characteristics of the reaction intermediates*

The notion of the "chemical potential" appears to be of paramount importance in analysing the role of the reaction intermediates in catalytic processes.

Note first of all that for the steady occurrence of a catalytic reaction, the chemical transformations of a complex between the reagent and the reaction site occur between the actual values of the chemical potential of the reaction intermediates rather than between the "bottoms" of the corresponding energy potential curves (see Fig. 5). For catalysis on a single active centre, this leads to the conclusion that *the rate of reaction is independent of the standard thermodynamic parameters of the intermediate species* this statement being rigorously valid in the case of small relative populations of the active centres by the intermediate complexes. In addition to the proportionality of this rate to the difference in thermodynamic rushes of the initial reagent and the final product, the rate appears to be proportional to the thermodynamic rush of the "free" form of the active site as well as being *dependent only on the standard thermodynamic parameters of the transient states* (in an ideal situation, see Section 3). In the above ideal situation, the dependence of the steady-state rate on the standard thermodynamic characteristics of the intermediates exists only for a significant population of the catalytic sites with the reaction complexes. This dependence is expressed as a term in the denominator in the equation for Langmuir adsorption; anyhow, the steady-state values of chemical potential μ_i of intermediates are dependent on only the values of ϵ_{ij} and $\mu_{\mathrm{R+K}}$, $\mu_{\mathrm{P+K}}$ only.

The chemical potentials of all catalytic intermediates in a steady-state situation *should drop stepwise* in the direction of the final product *and lie between* those of the initial reagents and the final products. Thus, any chemical transformations of the intermediates occurs from these steady-state energy levels. One can say that the intermediates "accumulate" the Gibbs energy of the main reaction by increasing their stationary chemical potential (e.g., via an increase of their concentration) to a level controlled by the "reduced" rate constants ϵ_{ij} of the chemical reactions between the intermediates, or in other words, by the standard chemical potentials of the transient states only.

The reason for the above "strange" behaviour of catalysts is due to the independence from the mentioned characteristics of the chemical potentials of both intermediates and (at low coverage) the "free" form of the active centre.

The above statements are easily demonstrated by analysis of the simplest scheme

$$\mathrm{R} + \mathrm{K} \overset{\epsilon_1}{\rightleftarrows} \mathrm{AK} \overset{\epsilon_2}{\rightleftarrows} \mathrm{P} + \mathrm{K}.$$

Evidently, the overall reaction rate in the steady state is expressed as

$$V_{\sum} = \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} (\tilde{n}_{\mathrm{R}} - \tilde{n}_{\mathrm{P}}) \tilde{n}_{\mathrm{K}}.$$

A dependence on standard characteristics of the intermediate AK arises only through the relation for the concentrations of different forms of the reaction sites

$$[AK] + [K] = [K_0],$$

which can be reformulated into the corresponding relationship for thermodynamic rushes

$$\lambda \tilde{n}_{\mathrm{AK}} + \tilde{n}_{\mathrm{K}} = \tilde{n}^0_{\mathrm{K}}.$$

Here $[K_0]$ is the total concentration of reaction sites, $\tilde{n}^0_{\mathrm{K}} = [K_0] \exp(\mu^0_{\mathrm{K}}/RT)$, $\lambda = \exp[(\mu^0_{\mathrm{K}} - \mu^0_{\mathrm{AK}})/RT$, and μ^0_{K} and μ^0_{AK} are the standard chemical potentials of the free form of the reaction centre and of AK, respectively. Since

$$\epsilon_1 (\tilde{n}_{\mathrm{R}} \tilde{n}_{\mathrm{K}} - \tilde{n}_{\mathrm{AK}}) = \epsilon_2 (\tilde{n}_{\mathrm{AK}} - \tilde{n}_{\mathrm{P}} \tilde{n}_{\mathrm{K}}),$$
$$\text{and} \quad \tilde{n}_{\mathrm{AK}} = \tilde{n}_{\mathrm{K}} (\epsilon_1 \tilde{n}_{\mathrm{R}} + \epsilon_2 \tilde{n}_{\mathrm{P}})/(\epsilon_1 + \epsilon_2),$$

$$V_{\sum} = \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} (\tilde{n}_{\mathrm{R}} - \tilde{n}_{\mathrm{P}}) \frac{\tilde{n}^0_{\mathrm{K}}}{1 + \lambda(\epsilon_1 \tilde{n}_{\mathrm{R}} + \epsilon_2 \tilde{n}_{\mathrm{P}})/(\epsilon_1 + \epsilon_2)},$$

i.e. a dependence on μ^0_{AK} via λ appears only in cases in which the intermediate AK exists in large fractions in comparison with that of the free form K.

For an arbitrary situation expressed via scheme (5)

$$V_{\sum} = \epsilon_{\mathrm{eff}} (\tilde{n}_{\mathrm{R}} - \tilde{n}_{\mathrm{P}}) \tilde{n}_{\mathrm{K}} = \epsilon_{\mathrm{eff}} (\tilde{n}_{\mathrm{R}} - \tilde{n}_{\mathrm{P}}) \times \frac{\tilde{n}^0_{\mathrm{K}}}{1 + \sum_i \phi_i \tilde{n}_{\mathrm{R}} + \sum_i \psi_i \tilde{n}_{\mathrm{P}}}, \tag{6}$$

where parameters ϕ_i and ψ_i are algebraic combinations of parameters such as λ and ϵ (see [21]).

A particular scheme of sequential transformations of a catalytic intermediate, which can be reduced in some cases (e.g., at very slow rates of migration of the absorbed species) to monomolecular transformations, is shown in Fig. 6.

Generally, the occurrence of simple catalytic reactions with a set of possibilities for intermediates can be visualized by "mountains", i.e. transient states separated by "lakes" with their surface levels corresponding to the steady-state values of chemical potentials of the intermediates (see Fig. 7).

Note that the above conclusion on the absence of a significant dependence of the steady-state rate on the standard thermodynamic parameters of the intermediate complexes does not, however, exclude the possibility of a dependence through the existence of some natural correlation between ϵ_{ij} values and the energies of the intermediates. Such experimentally observed correlations have been discussed, for example, in [5], and their respective interpretations via the joint kinetic–thermodynamic analysis are given in [21]. Interestingly enough, the above argument can cause quantum chemists to reformulate some conclusions of their calculations, these being directed mostly to the determination of the standard thermodynamic parameters of the intermediates.

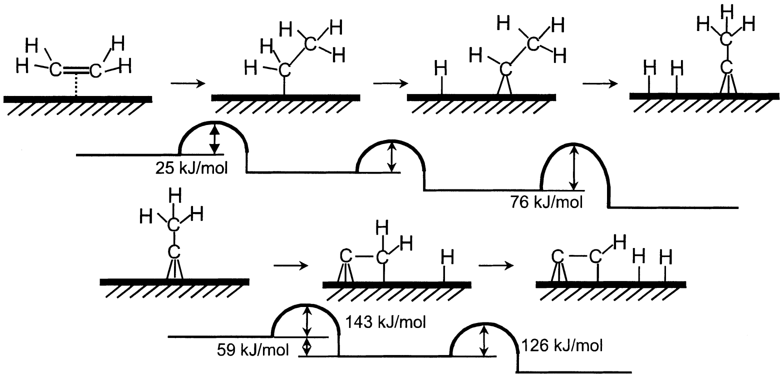

Fig. 6. An example of sequential evolutions of a complex reactant–reaction centre for the conversion of an adsorbed molecule of ethylene to ethylidyne (CCH_3) and further fragmentation of the ethylidyne to give vinylidene (CCH_2) and acetylide (CCH) on Pt(1 1 1). Note that the energetics of the transformations are given for the "classic" kinetic schemes (compiled from [22]).

4.5. *Concept of "transient state" for transformations of a reaction complex on a catalyst active site*

From the above conclusions, it follows immediately that the concept of the "transient state" in catalysis may be much more sophisticated and more broadly applicable than that in conventional "collisional" chemical kinetics. For example, in catalysis this state may include not only "virtual" non-thermalized transient states but also a large set of "shallow" thermalized intermediates allowing a complicated "monomolecular" dynamic evolution of the complex "reagent–active centre" (see Fig. 8). Indeed, the behaviour of such an "extended" transient state does not differ from the behaviour of the "true" transient state since it can be characterized by a single parameter ϵ_{eff} only (see expression (6)); the "real shallow"

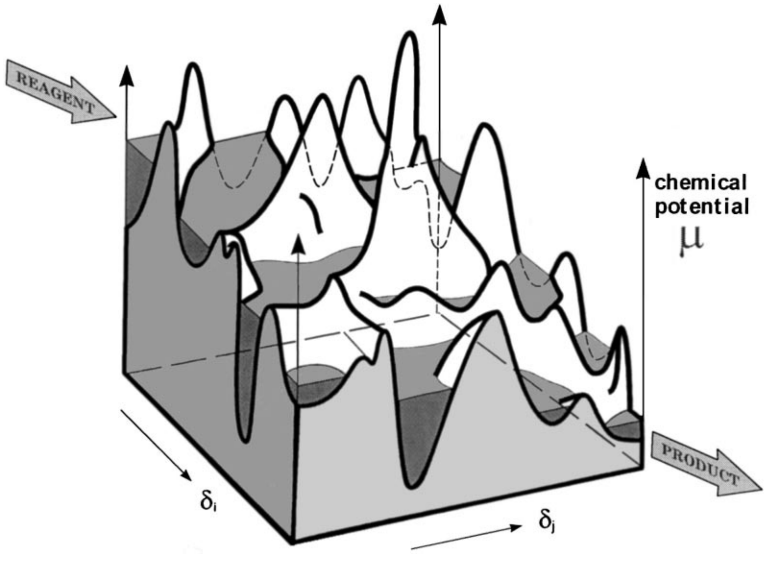

Fig. 7. World of "mountains" and steady-state "lakes" for the transformation of a complex between a reagent and an active site of a catalyst. The levels of the steady-state lake surfaces drop stepwise from the reagent to the product.

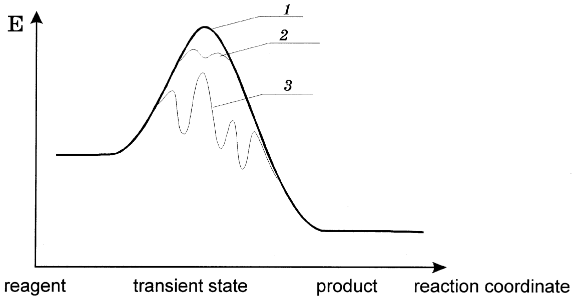

Fig. 8. A specificity of notion of the transient state in catalysis. Curve (1) corresponds to the situation when the path along the reaction coordinate has only one virtual non-thermalized transient state, while curves (2) and (3) correspond to the situation when the path along the reaction coordinate is going through one or more real thermalized shallow intermediates.

type of the intermediates ensures the absence of significant corrections in the denominator of expressions such as Eq. (6).

The above extension of the concept of "transient state" seems to allow a resolution of some problems connected to a quantitative, rather than a qualitative difference in the traditional definition of "stepwise" and "coupled" mechanisms of catalysis [5] as well as in an assumed necessity of different types of synchronizations in the dynamic evolution of the reaction complex. One can assume that the above extended interpretation of the transient state will also be useful when analysing the influence of not too strong intermediate interactions of the adsorbed reactant molecules. For example, this can resolve a long-term discussion on whether intermediate carbocations inside, say, zeolites cavities are real or virtual structures. Following the language of the above extended concept of the transient state, one can proceed continuously from one situation to another, in which the parameter ϵ_{eff} is to be changed continuously when new thermalized intermediate states are showing up. Note also that shallow intermediates usually cannot be detected by conventional physical methods due to their small concentrations compared with much larger concentrations of the initial state of the reaction site. Therefore, speculations on the general existence of shallow intermediates will continue to be discussed due to limited possibilities for their experimental observation.

4.6. *Modified Onsager equations for parallel catalytic transformations with the joint intermediates*

One can make a further generalization of the Horiuti–Boreskov rule and show that in the case of a set of parallel mutually interacting catalytic reactions, their steady-state rates can be expressed by Onsager-type equations. However, instead of the affinities of the above reactions, which are considered to be the driving thermodynamic forces for the dynamic evolution of the system these modified equations should use the respective differences in the "thermodynamic rushes" as the actual thermodynamic forces generating the respective fluxes of thermodynamic parameters. In our case, these fluxes are the rates of formation of the corresponding product through a particular channel in the complex chemical process.

This statement is easily demonstrated when considering, for example, the simplest example of two parallel catalytic processes

$$\mathrm{A} \rightleftarrows \mathrm{B}$$

$$\mathrm{A} \rightleftarrows \mathrm{C} \tag{7}$$

with the formation of the main product B and the by-product C out of one initial reagent A.

Indeed, when the reaction occurs through a joint intermediate AK:

$$\mathrm{A} + \mathrm{K} \overset{\epsilon_1}{\rightleftarrows} \mathrm{AK}, \quad \mathrm{AK} \overset{\epsilon_2}{\rightleftarrows} \mathrm{B} + \mathrm{K}, \quad \mathrm{AK} \overset{\epsilon_3}{\rightleftarrows} \mathrm{C} + \mathrm{K}, \tag{8}$$

a simple mathematical procedure [23] shows that for the steady-state occurrence of these reactions, the expressions for the steady rates are

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = L_{11}(\tilde{n}_{\mathrm{A}} - \tilde{n}_{\mathrm{B}}) + L_{12}(\tilde{n}_{\mathrm{A}} - \tilde{n}_{\mathrm{C}}),$$
$$\frac{\mathrm{d}C_{\mathrm{C}}}{\mathrm{d}t} = L_{21}(\tilde{n}_{\mathrm{A}} - \tilde{n}_{\mathrm{B}}) + L_{22}(\tilde{n}_{\mathrm{A}} - \tilde{n}_{\mathrm{C}}),$$

with the Onsager coefficients

$$L_{11} = \frac{\epsilon_1\epsilon_2 + \epsilon_2\epsilon_3}{\epsilon_1 + \epsilon_2 + \epsilon_3}\tilde{n}_{\mathrm{K}} > 0, \quad L_{22} = \frac{\epsilon_1\epsilon_3 + \epsilon_2\epsilon_3}{\epsilon_1 + \epsilon_2 + \epsilon_3}\tilde{n}_{\mathrm{K}} > 0,$$
$$L_{12} = L_{21} = -\frac{\epsilon_2\epsilon_3}{\epsilon_1 + \epsilon_2 + \epsilon_3}\tilde{n}_{\mathrm{K}}.$$

Thus, in a more general case, this situation corresponds directly to the modified Onsager equations for coupled catalytic reactions

$$v_i = \frac{d[P_i]}{dt} = \sum_j L_{ij} X_j = \sum_j L_{ij}(\tilde{n}_R - \tilde{n}_{P_j}),$$

with $L_{ii}>0$, $L_{ij}=L_{ji}$ and $[P_i]$ the concentration of the product P_i.

Note that expressions such as (9) are of importance for studying the behaviour of complicated chemical systems with unknown mechanisms of "internal" transformations: these mechanisms are reflected in the relative values of coefficients L_{ij} only. The sign or absence of thermodynamic forces X_j indicate the tendency for the system to evolve in a particular direction.

Two additional important conclusions follow from the above consideration:

1. The statement on the absence of an influence of a catalyst on a system being in the thermodynamic equilibrium between the reagents and products *is not valid in general.* This statement is valid only when either *100% selectivity* of the catalyst with respect to the equilibrized transformation or when there is a *complete* equilibrium in the reaction mixture. Both conditions practically never take place in real systems. The above conclusion seems to contradict what is taught in elementary courses in catalysis but originates directly from the existence of numerous thermodynamic forces acting in a non-selective or non-equilibrized system and causing parallel transformations. A more accurate and sophisticated statement on the general behaviour of catalysts is therefore needed instead of the well-known simple claim that "a catalyst is not able to disturb thermodynamic equilibrium".
2. The selectivity of catalytic reactions can be significantly changed by actively changing the chemical potential of the byproducts of the reaction. Moreover, in some cases it is possible even to reverse the direction of the parallel reactions and therewith to utilize some kinds of byproducts rather than producing them.

It is remarkable that until now there have been only few discussions on the possibility *of changing the selectivity* or even *the direction* of the parallel catalytic processes in case that the "main" and "side" reactions have the same catalytic intermediate. This possibility follows directly from analysing the actual stationary values of chemical potentials of the catalytic intermediates as well as the reagents, the products and byproducts of the overall catalytic reactions. Evidently, the above phenomena have a "threshold" nature in respect to the concentration of the byproduct. A graphical interpretation of this conclusion is shown in Fig. 9. Note that for case (a) in Fig. 9 the reverse of the transformation of the byproduct C can be initiated when $\mu_C>\mu_A$ while in case (b) it will occur when $\mu_C>\mu_{AK}-\mu_K$; this latter condition is indeed milder since everywhere $\mu_{AK}-\mu_K<\mu_A$. An evident practical importance of this conclusion is a principal possibility to derive more correct conditions than

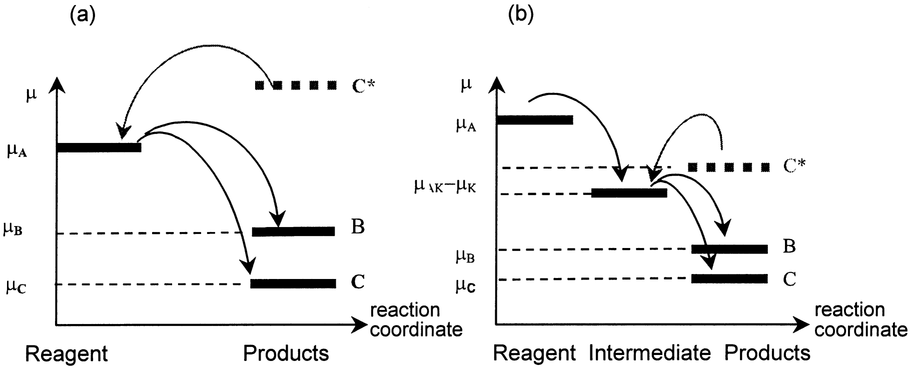

Fig. 9. Thermodynamic coupling of parallel reactions (7) in case of the absence (a) and the presence (b) of joint catalytic intermediates. For the case (b), scheme (8) is accepted. Marks C^* show a situation when the rate of the side reaction starts to change its direction and contributes to generation of the main product B.

one can derive from simple "equilibrium thermodynamics" for the direction of the co-occurrence of many processes with common intermediates. Examples of such processes are coke deposition, involving light molecules (e.g., CO_2, CH_4, etc.) and the involvement of the carbon in direct reactions with larger hydrocarbons, etc.

A particular example of a complicated application of the above thermodynamic coupling analysis is the analysis of the conditions for carbon deposition on a catalyst during reforming of methane with carbon dioxide. This deposition is commonly discussed as a consequence of parallel transformations such as

$$CH_4 + CO_2 \rightleftarrows 2H_2 + 2CO$$

$$CH_4 \rightleftarrows C + 2H_2$$

$$C + CO_2 \rightleftarrows 2CO$$

Let us assume that these reactions occur through two inter-related C_1-intermediates, X_1 and X_2:

$$CH_4 + K \overset{\epsilon_1}{\rightleftarrows} X_1 + H_2$$

$$X_1 \overset{\epsilon_2}{\rightleftarrows} X_2 + H_2$$

$$X_2 \overset{\epsilon_2}{\rightleftarrows} K + C$$

$$X_2 + CO_2 \overset{\epsilon_4}{\rightleftarrows} 2CO + K$$

Performing the joint kinetic–thermodynamic analysis, we find that in the steady state with respect to both X_1 and X_2, the condition for coke deposition will be

$$\epsilon_1\epsilon_2(\tilde{n}_C \cdot \tilde{n}_{H_2}^2 - \tilde{n}_{CH_4}) + (\epsilon_1\tilde{n}_{H_2} + \epsilon_2)\epsilon_4(\tilde{n}_C \cdot \tilde{n}_{CO_2} \cdot \tilde{n}_{CO}^2) < 0. \qquad (10)$$

This condition differs significantly from the two corresponding conditions following from the conventional "equilibrium thermodynamic" analysis:

$$\tilde{n}_C \cdot \tilde{n}_{H_2}^2 < \tilde{n}_{CH_4}, \quad \tilde{n}_C \cdot \tilde{n}_{CO_2} < \tilde{n}_{CO}^2,$$

which are consequences of two straightforward inequalities $\mu_C + 2\mu_{H_2} < \mu_{CH_4}$ and $\mu_C + \mu_{CO_2} < 2\mu_{CO}$ (see e.g. [24]). It is more difficult to satisfy simultaneously both the latter conditions than to satisfy one condition given by expression (10).

5. Equilibrium and non-equilibrium reconstruction of the catalyst surface: experimental evidence for the existence of stable non-equilibrium steady state of heterogeneous catalysts

Interaction of the reaction medium with the catalyst results inevitably in a reconstruction of the catalyst surface. However, it has only very seldom been recognized that one should distinguish *equilibrium* and *non-equilibrium* reconstruction. The first type of reconstruction corresponds to the adjustment of the surface to the reaction medium in cases when there are no driving forces for the "coupling" reactions and the catalyst condition therefore corresponds to the equilibrated composition of the medium. The second type of reconstruction is driven by the thermodynamic forces of the catalysed "coupling" reaction.

5.1. Equilibrium reconstruction of catalysts

A particular example of such an *equilibrium reconstruction* is the well-known process of reconstruction of the surfaces of metal monocrystals such as in the microfaceting of Pt(1 0 0) under the influence of CO, or the creation of oxide surface phases on Ni(1 1 1) under the influence of O_2 (see e.g. [22]). Less well known are interesting recently observed phenomena such as the reversible migration of Cu and H atoms on copper-containing oxide catalysts under conditions of mild reduction with H_2.

Copper-containing oxide catalysts are widely used for methanol synthesis and related processes and therefore have been investigated actively by numerous physical methods. One of the peculiarities observed for such catalysts is the absence of a detectable amount of metallic copper in initially prepared catalysts as well as in used catalysts under ambient conditions. However, metallic copper has regularly been observed in in situ studies of these catalysts during their operation in reductive media at elevated temperatures. Recently, by implementation of direct in situ methods, it has been concluded that the above peculiarity is the result of a *reversible* reconstruction of the catalyst under the action of hydrogen from the reaction medium. Indeed, the presence of H_2 at elevated, but still not very high temperatures, generates a reversible migration of copper cations from the bulk of

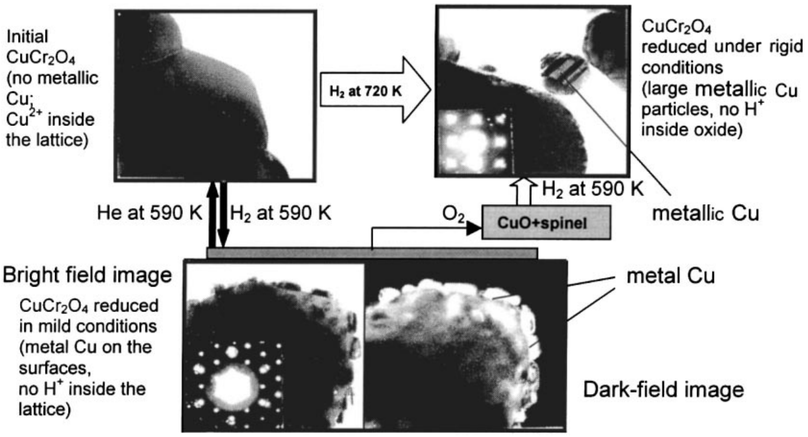

Fig. 10. An example of an "equilibrium" reversible reconstruction of a catalyst: reversible migration of copper ions and atoms in $CuCr_2O_4$ catalyst under mild (T=590 K) conditions as observed by TEM [25,26]. Reduction under more rigid conditions (two right paths of the transformations) results in an irreversible formation of large metallic Cu particles.

the oxide catalyst to the surface and reduction of these cations to metal nanoparticles (see Fig. 10 and [25,26]). The removal of copper cations from the oxide lattice is compensated by counter-migration of H^+ cations back into the bulk. Note that this process of ion migration should be attributed to equilibrium reconstruction since it does not need the occurrence of the catalysed reaction.

In homogeneous catalysis, equilibrium reconstruction corresponds to the equilibrium solvation of reaction centres and to the creation of equilibrized complexes of these centres with the reactants.

5.2. *Non-equilibrium reconstruction of catalysts*

From the viewpoint of this paper, the well-established examples of non-equilibrium reconstruction are of much greater interest than those of equilibrium reconstruction. Phenomena of non-equilibrium reconstruction have been discussed to date most commonly for non-stable steady states of the catalyst surface, isothermal oscillating chemical reactions and surface chemical waves.

In the case of *stability of the steady state of the catalyst*, the manifestation of non-equilibrium conditions due to the influence of the reaction medium (by "thermodynamic forces") is less known. The best known is its manifestation in homogeneous catalysis since the concentration of the reaction intermediates during such a process can hardly be the same as for an equilibrized system.

In a more general case, one also can expect that:

- there occurs a diminishing of the chemical potentials (concentrations) of the most active forms of the reaction centre (including those of the intermediates) and an increase of the chemical potentials (concentrations) of non-active forms in comparison with their chemical potentials (concentrations) under conditions of thermodynamic equilibrium of the reaction mixture with the same concentration of the initial reagents;
- there is a "non-equilibrium" reversible reconstruction of the catalyst surface;
- a displacement of the phase equilibria of the substance of the active component of the catalyst can be seen;
- there is the appearance of metastable "spacial" dissipative structures either on the catalyst surface or inside the active component;
- there is a difference between the actual temperature of the reaction centre from that of the ambient and of the bulk of the catalyst grain [27,28].

The steady state of the catalytic substance can differ significantly from the conventional equilibrium state of the same substance given by conventional equilibrium thermodynamics. For example, the catalyst can be in a *steady "metastable" state* (oversaturated, melt,

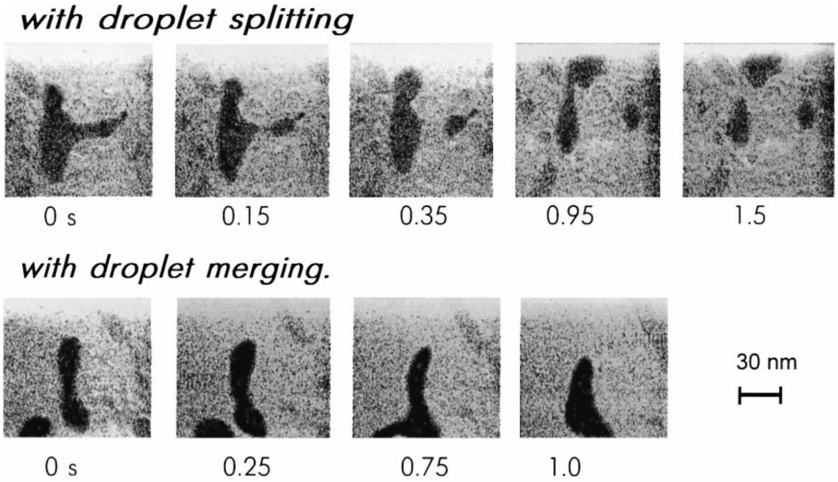

Fig. 11. Electron microscopic "in situ" videotape of the migration of Fe–C fluidized particles over an amorphous carbon support at 650°C (according to Krivoruchko et al. [29]).

etc.) or even create a "spacial dissipative structure". In some cases, one can predict, and experimentally observe, a shift in the position of the "coexistence curves" on the "*P–T* diagrams" for phase equilibria of the catalyst active component of mutually coexisting and interacting phases.

An example of experimental in situ observations of the formation of such a metastable state is the melting of the active components of metals like Fe, Ni, or Co operating as catalysts with the formation of carbon–metal solutions. Such melting at very low temperature has been recently observed during catalysing a transformation of amorphous carbon to graphite (see [29,30] and Figs. 11 and 12). In these studies, a set of transformations of transition metal hydroxides during their heating on the surface of amorphous carbon in vacuum were observed with the use of in situ TEM. The transformations correspond to reactions brought about by dissolution of carbon in the metal nanoparticles formed:

$$\begin{aligned}&\alpha\text{-FeOOH}, \mathrm{Co(OH)_2}, \mathrm{Ni(OH)_2}\\ &\quad \xrightarrow[\mathrm{C}]{300\text{–}450^\circ\mathrm{C}} \text{defect } \mathrm{Fe_3O_4}, \mathrm{CoO}, \mathrm{NiO}\\ &\quad \xrightarrow[\mathrm{C}]{t>600^\circ\mathrm{C}} (\mathrm{Fe-C})_{\mathrm{LL}}, (\mathrm{Co-C})_{\mathrm{LL}}, (\mathrm{Ni-C})_{\mathrm{LL}}.\end{aligned}$$

An interesting peculiarity of these transformations is that the smallest nanoparticles formed (with size $\leq$30–40 nm) behave at temperatures over 600°C completely as if they are liquid-like (see Figs. 11 and 12(a)), while the larger particles remain immobile (Fig. 12(b)).

The experimentally determined melting temperatures of the steady-state "carbon-in-metal" solutions are summarized in Table 1. They appear to be much lower than even those for known eutectics of carbon–metal solutions. For example, for carbon–iron liquid-like nanoparticle, the melting temperature can be 500°C lower than that of Fe–C eutectics.

According to Parmon [31], the formation of the above liquid-like particles should be considered as a first example of a direct in situ observation of a stable non-equilibrium steady state of the operating active centres in heterogeneous catalysts.

The above peculiarity in the behaviour of carbon–metal nanoparticles over amorphous carbon can be easily understood by assuming the formation of metastable supersaturated solutions of carbon in Fe, Co,

Table 1
Melting temperatures (°C) of both the pure metal and the metal–carbon eutectics as well as the temperature of formation of the steady liquid-like state of the active components of the catalysts (according to Krivoruchko and coworkers [29,30])

Metal	Pure	Eutectics with C	Steady state
Fe	1539	1145	640
Co	1493	1320	600
Ni	1453	1318	670

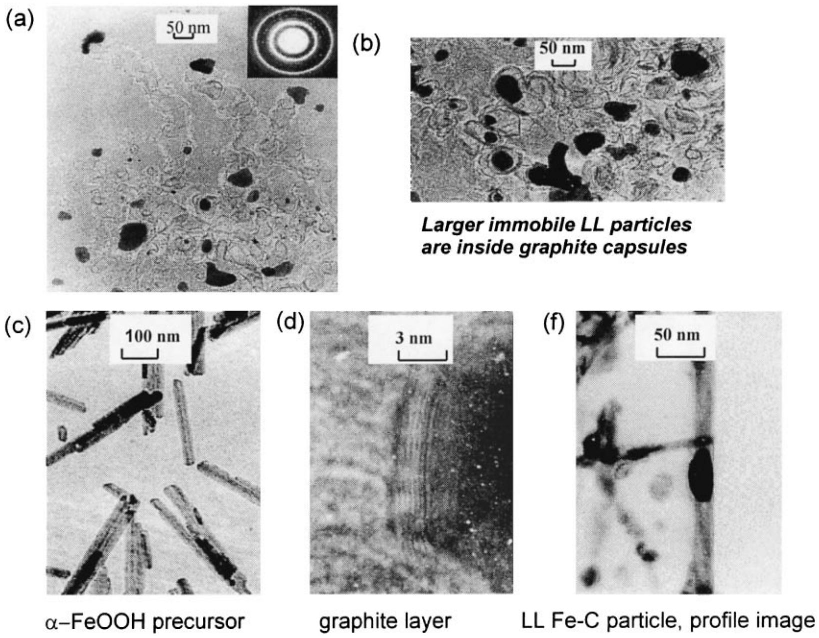

Fig. 12. Liquid-like Fe–C particles on an amorphous carbon film and the graphite tracks produced as observed during the reaction $C_{amorph} \rightarrow_{Fe} C_{graphite}$ (according to Krivoruchko and coworkers [29,30]). Note that pictures (a), (b), and (f) were taken at a temperature of 640°C.

and Ni during the catalytic graphitization of amorphous carbon.

Note, first of all, that the reaction

$$C_{amorph} \underset{met}{\rightarrow} C_{graphite}$$

occurs in a manner shown in Fig. 13. The reaction is driven by a quite large affinity for the carbon transformation $A = -\Delta_r G \approx 12$ kJ/mol which is much larger than RT.

Since during the graphitization, the steady-state value of the chemical potential μ_C of carbon in the carbon–metal solution should obey the rule $\mu_C(\text{amorf}) > \mu_C(\text{in metal}) > \mu_C(\text{graphite})$, it follows that the steady-state concentration of carbon in the metal has to be much higher than the concentration of carbon in the stable eutectics. In the last case, an eutectic means the equilibration of the dissolved carbon with graphite, rather than with more energetic forms of carbon.

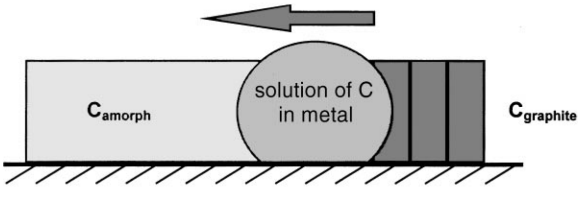

Fig. 13. Schematic representation of the fluidization of a nanoparticle of a catalytically active metal during the graphitization of amorphous carbon. The upper arrow shows the direction of the movement of the metal–carbon droplet.

In the case of the rate limiting step (see Section 4.1) for the catalytic graphitization being the formation of graphite slices from dissolved carbon, the concentration of dissolved carbon in metal should be much higher than when the metal is in contact with graphite. The concentration of the dissolved reactive carbon can be estimated assuming equilibrium with the amorphous carbon [31]:

$$[C]_{\text{amorph}} = [C]_{\text{graphite}} \exp(-\Delta_r G/RT) \approx 4[C]_{\text{graphite}}.$$

Here $[C]$ is the carbon concentration in the metal solution while $\Delta_r G$ is the difference in the Gibbs energies of amorphous carbon and graphite. According the Schröder relation, it is easy to estimate the expected melting temperature of the solution:

$$\ln(1 - X_C) = -\frac{\Delta_m H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

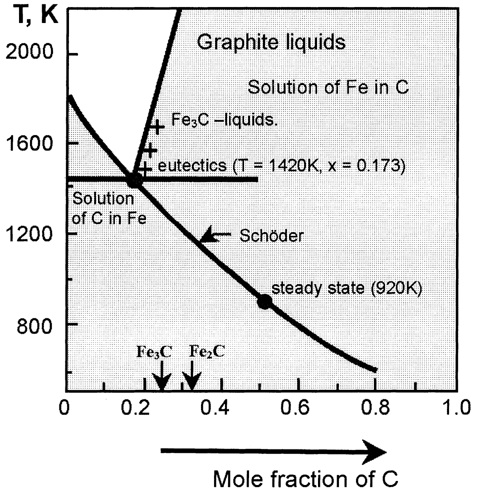

Fig. 14. A simplified version of the metastable phase equilibrium for the Fe–C system during the occurrence of the catalytic graphitization of amorphous carbon. Fe_3C and Fe_2C represent the stoichiometric iron carbides.

where T_0 is melting temperature for the pure metal, T is that for the metal–carbon melt with a carbon mole fraction X_C and $\Delta_m H$ is the heat of melting of the pure metal. Since the parameters for the stable common eutectics are well known (see Fig. 14), one obtains the result that the magnitude of the decrease of the melting temperature of the operating metal nanoparticles should be up to 500–900°C compared to the common eutectics. This is equivalent to what was observed in situ. One should take into consideration that, in addition to the large cryoscopic effect due to the metal particle supersaturation with carbon, there are also at least two extra ways to influence the melting temperature of the active components of the catalyst. Firstly, there is the well-known influence of the particle size r, that tends to reduce the melting temperature of small nanoparticles

$$T_r = T_\infty \exp\left(\frac{-2\sigma V_m}{r\Delta_m H}\right),$$

and secondly, there is an influence of the size r' of the crystallization centres on the supersaturation needed in order to initiate crystallization of the dissolved substance

$$x_{r'} = x_\infty \exp\left(\frac{2\sigma' V_m}{r' RT}\right).$$

Here σ is the surface tension and V_m is the molar volume of the metal. The symbol ∞ relates to the flat surface.

Recently, from the point of view of supersaturation of metal with carbon, we have considered the formation of carbon nanotubes over Co-containing catalysts during CO disproportionation [32]:

$$2CO \overset{Co^0}{\rightarrow} C + CO_2$$

When studying the reaction over a wide range of conditions, it was found that graphite crystallites of two different morphologies are formed in the process, these depending on the diameter of the metal cobalt particles.

Samples containing particles of the cubic phase of (β-)Co^0 of various diameters (from 5 to 500 nm) were treated in a CO flow at temperatures of up to 800°C; thermogravimetry in situ was applied to reveal the actual processes occurring during this treatment. The treated samples were tested by XRD and high resolution electron microscopy techniques. On increasing the temperature in the CO atmosphere, disproportionation of the CO to CO_2 and elementary carbon was observed at temperatures as low as 290°C. Three distinct temperature regions were distinguished, these differing is the nature of the transformations of the resulting elementary carbon:

1. In the range 300–350°C, adsorbed carbon atoms dissolved in the Co^0 particles, leading to the formation of highly defective Co^0 particles. Their structure seems to be intermediate between that of cubic (β) and hexagonal (α) cobalt.
2. In the range 350–450°C (with a maximum rate at 420°C), the formation of thick graphite shields (so-called "shells" of more than 10 nm in width) occurred, these covering the metal nanoparticles.
3. In the range 450–750°C (with a maximum rate at 580–620°C), the reaction led to the formation of thin carbon nanotubes with an outer diameter of about 10 nm and an inner diameter of 3.0 nm.

It was found that the formation of graphite crystallites with two different morphologies depends on the diameter of the Co^0 particle. The "egg-shell" graphite phase is formed over the relatively large Co^0 particles at temperatures between 300°C and 450°C, causing rapid deactivation of the catalyst, while the nanotubes

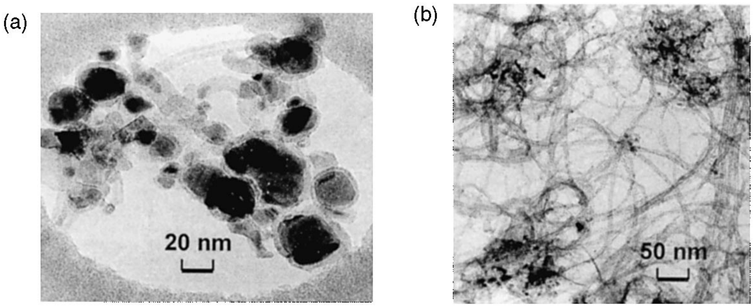

Fig. 15. Micrographs of carbon generated during the CO disproportionation by ‘‘large’’ (a) and ‘‘small’’ (b) cobalt particles. The ‘‘large’’ particles (of a diameter more than 250 Å) form the graphite phase with ‘‘egg-shell’’ morphology covering the surface of the particle. The ‘‘small’’ ones (of a diameter less than 250 Å, about 100 Å for the sample studied) give rise to the formation of thin carbon nanotubes with an outer diameter approximately equal to the diameter of the Co^0 particle and the wall thickness of ca. 30–50 Å (according to Khassin et al. [32]).

formed over the comparatively small particles at higher temperatures (see Fig. 15).

A simple thermodynamic analysis [32], analogous to that given above, shows that disproportionation of CO also seems to proceed through the formation of a supersaturated solution of C in metallic Co as in the case of fluidization of metal particles during the graphitization of amorphous carbon. It is possible to show for the case of CO disproportionation that the limiting concentration of carbon in the metal depends on the maximum size of the graphite crystallite being formed. The large cobalt particles (diameter ca. 25 nm) behave as large nuclei for carbon crystallization. Its limiting concentration is therefore low enough to lead to the formation of graphite at low temperatures and to give deactivation of the active component due to carbon shielding. For small particles, the limiting concentration of dissolved carbon is high and so the fluidized state of the carbon-in-metal supersaturated solution is formed. This leads to a dramatic change of the catalytic properties of the cobalt particles and prevents deactivation of the mobile fluidized active particles. As a result, long carbon nanotubes can be formed.

A quantitative analysis of the thermodynamic equilibria of systems involving primary amorphous-like solutions of C in the metal and of graphitic carbon solutions in the metal together with analyses of the experimental data give rise to the assumption that fluidization of the ‘‘small’’ metal particles due to the formation of supersaturated solutions of carbon may occur not only during graphitization of amorphous carbon or CO disproportionation, but also during pyrolysis of lower hydrocarbons according to the

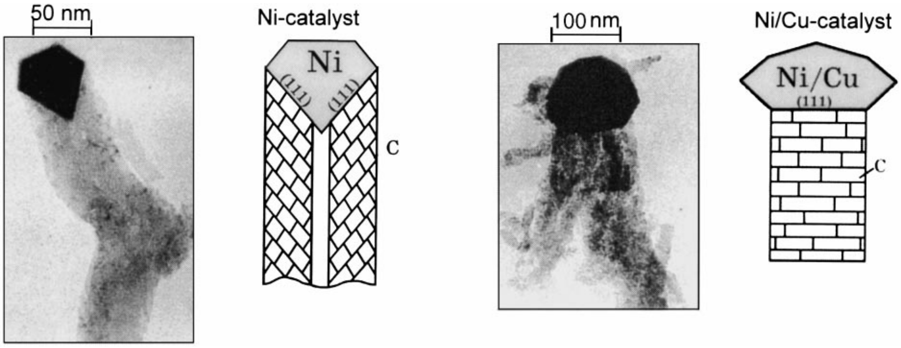

Fig. 16. The formation of filamentous carbon obtained (together with hydrogen) during the medium temperature catalytic pyrolysis of methane and lower hydrocarbons via reaction (11) (according to Likholobov et al. [33]).

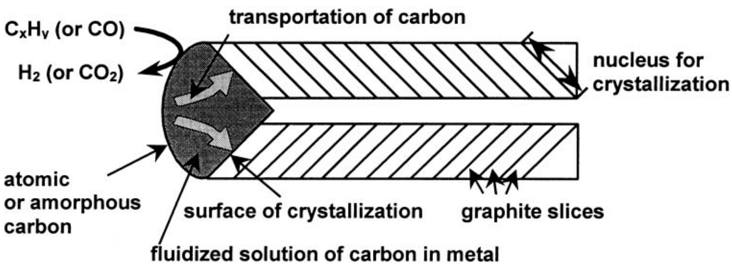

Fig. 17. A possible mechanism for the formation of carbon filaments during the catalytic pyrolysis of light hydrocarbons or CO disproportionation.

reaction

$$C_nH_m \underset{450-650^\circ C}{\overset{\text{catalysts}}{\longrightarrow}} nC\downarrow + \frac{m}{2}H_2\uparrow \qquad (11)$$

The above reaction is sometimes also accompanied by the formation of carbon filaments (see Fig. 16). Note that the weight of the catalyst during such stable catalytic processes can increase by a factor of 300 as a consequence of formation of the pure carbonaceous filamentous material [33].

A stable fluidized state of the supersaturated solution of carbon in a metal seems to be responsible for the formation of carbon filaments and nanotubes in a large set of processes as well as graphitic carbon deposition via the formation of primary atomic carbon or another kind of energetic carbon particles on the surface of the catalytically active metal (see Fig. 17). Note that the formation of typically observed "fish bones" structure of the carbon filaments or nanotubes formed is easily understood as a consequence of possible pulsations during the graphite crystallization [31]. Note also that the growth of carbon filaments and nanotubes corresponds to the diffusion of carbon through the active component with a diffusion coefficient of $D \gg 10^{-10}$ cm^2/s. This very high rate of carbon diffusion through the metal particle is also consistent with the fluidized state of the metal.

We have recently also observed the creation of a kind of spacial dissipative structure inside active components of metal cobalt catalysts during the above intensive reaction of CO disproportionation [32]. This metastable structure exhibits regular microscopic layers of different crystalline phases of cobalt (see Fig. 18). Note that such layering can never be obtained in thermodynamically equilibrium conditions and that it therefore appears to correspond to the formation of spacially dissipative structures.

6. Conclusion

The above discussion shows that the role of non-equilibrium thermodynamics in creating a physico-

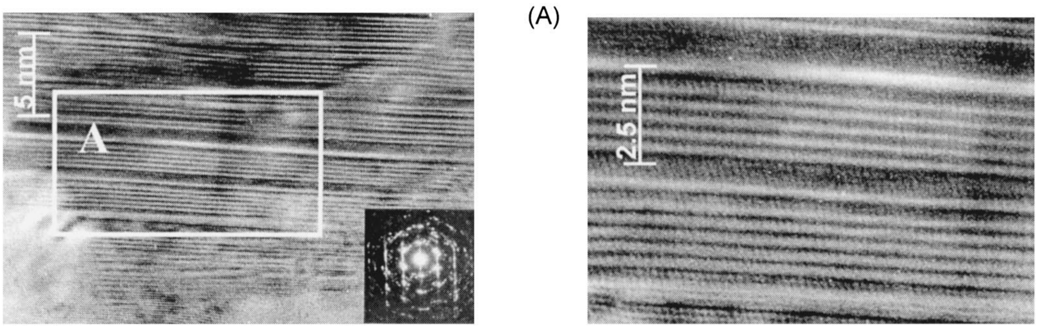

Fig. 18. Observation of a regular layering inside cobalt particles with size >200 Å after their exposure to 1 bar of CO at a temperature of 700 K. White zones are thin layers (ca. 5 atoms thick) of hexahonal Co^0, while the dark zones are thin layers of cubic Co^0. The right-hand pattern is a twofold magnification of the section A.

chemical background for heterogeneous catalysis is in fact much more embracing and interesting than that given by equilibrium thermodynamics or simply by Boreskov's rule or the concept of invariant thermodynamic equilibria in the presence of catalysts.

To date, many of the possible thermodynamic peculiarities of the non-equilibrium, steady state of catalysts, both stable and unstable, have already been observed in experimental in situ studies. However, a consecutive thermodynamic interpretation of the phenomena observed in situ is often still far from satisfactory.

An important tool for this method of interpreting and envisaging general phenomena seems to be a joint kinetic–thermodynamic analysis facilitated by an implementation of the ''thermodynamic form'' of the kinetic equations and the use of the actual values of the chemical potentials of the catalytic intermediates. From this analysis, it may be concluded that of primary importance for occurrence of catalytic processes are the values of the reduced rate constants ϵ_{ij}. These parameters involve the properties of the transient states between the different catalytic intermediates and they determine the stationary values of the chemical potentials of the catalytic intermediates. Thus, one should expect that for the sake of the future development of a successful theory of catalytic action, the important steps seem to be a systematization and extensive analysis of the possible (typical) catalytic transient states, i.e. the complex ''reactant–reaction centres'' undergoing monomolecular evolution under the action of internal driving forces. Studies of the possibilities of influencing or controlling states, as well as of predicting the ''reversible deactivation'' of the catalyst reaction centres due to the formation of stable intermediates are also of great importance. Moreover, this systematization and the structural–thermodynamic analysis of possible transient complexes appear to be the main tools for further advances in a general theory of catalysis supported by quantum chemistry.

There is also another set of generally important problems of catalysis which have to be solved at least partly in the framework of non-equilibrium thermodynamics.

For example, what is the particular nature of main driving forces controlling the dynamics of the surface reconstruction and removing the activation barriers for the occurrence of this process, and what are the situations in which a reversible surface reconstruction is to be expected? Have the main driving forces of the reconstruction simply an ''equilibrium'' thermodynamic nature (such as the creation of strong complexes between the surface atoms and some reactants, as in the case of some noble metals with ligands such as CO molecules) or do these depend on both the dynamic situation and the affinity of the catalysed reaction as well? The hope is that in the near future we will achieve significant success in answering these and other numerous general questions in catalysis.

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