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Communication

Rate Equations of Structure-Sensitive Catalytic Reactions with Arbitrary Kinetics

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Abstract: A general mathematical framework for the quantitative description of the cluster size dependence in heterogeneous catalytic reactions has been developed based on an analysis of the Gibbs energy of elementary reactions. The methodology was illustrated for a generic linear sequence of elementary reactions with three steps, a multi-step mechanism of ethanol oxidation comprising linear, nonlinear and quasi-equilibria steps and a network of parallel reactions in transformations of furfural.

Keywords: structure sensitivity; rate equations; parallel reactions; arbitrary kinetics

1. Introduction

A substantial effort has been put forward in recent years in the understanding structure-sensitive reactions, for which the turnover frequency (or the rate per exposed site) depends on the size of the metal cluster [1–6] increasing, decreasing or passing through a maximum. Such changes of turnover frequency (TOF) with the cluster size can originate from changes in the relative ratio between edges, corners and terrace atoms, which exhibit different reactivity or, because of other phenomena, influence reactivity, e.g., alterations of the electronic state or resistance to deactivation.

The treatment of structure sensitivity in [7] considered differences in the adsorption energy between edges and terraces, leading subsequently to different activities of edges and terraces in terms of reactivity. A linear free energy relationship was applied linking kinetics with thermodynamics. The initial treatment [7] and further expansions were limited to a two-step sequence and some selected mechanisms, such as the Eley–Rideal and the Langmuir–Hinshelwood [8–10]. For more complicated reaction mechanisms, such as a Christiansen sequence of all linear steps, apart from adsorption and desorption, the equilibrium constants as well as the rate constants in forward and reverse directions of other reaction steps were considered to be independent on the cluster size.

At the same time, the reaction mechanisms can contain not only linear but also nonlinear steps, thus making a derivation of the rate equations where the cluster size dependence is directly incorporated into the rate expressions, which is far from straightforward.

The intention of the current study is to provide a general framework for the derivation of kinetic expressions for multistep reaction mechanisms with linear and nonlinear steps and different adsorbed species on the surface.

The approach will be illustrated for a Christiansen sequence and a reaction mechanism comprising reversible, irreversible and quasi-equilibria steps. The same methodology can be applied for multi-route reactions as exemplified by a network of parallel reactions.

It should be noted that the kinetic expressions derived below rely on the direct collision model assuming that the surface diffusion of adsorbed species is fast. Moreover, in the treatment of this study, the relationship between the particle size and the structure of catalytic sites is considered to be constant, being independent of cluster size. In a more general case, the electronic states of the catalytic site may change when changing the cluster size, thus influencing the reaction kinetics and even the reaction mechanism.



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2. Theoretical Framework

Let us consider first an elementary reaction of the following type



Such a reaction can correspond to the dissociative adsorption of a molecule containing two atoms (e.g., O₂) in the presence of some species already present on the surface (e.g., hydroxyls).

The Gibbs energy of this step can be written

$$\begin{aligned} \Delta G_{reaction} &= \Delta G_{A,adsorbed} + \Delta G_{AB,adsorbed} - \Delta G_{A_2} - \Delta G_{catalyst} - \Delta G_{B,adsorbed} \\ &= \Delta G_{A,adsorbed} + \Delta G_{AB,adsorbed} - \Delta G_{B,adsorbed} \end{aligned} \quad (2)$$

as the Gibbs energy for the formation of the molecule A₂ is zero by definition.

Another example can be the recombination of two adsorbed atoms of a diatomic molecule passing through the molecular adsorbed state



The Gibbs energy for this reaction is obviously

$$\Delta G_{reaction} = \Delta G_{A_2,adsorbed} + \Delta G_{catalyst} - 2\Delta G_{A,adsorbed} \quad (4)$$

When only terraces and edges [7] are considered as sites with different reactivity, the Gibbs energy of reactions described by Equations (1) or (3) are expressed in the following way

$$\begin{aligned} \Delta G_{reaction} &= \Delta G_{reaction,terraces} f_{terraces} + \Delta G_{reaction,edges} f_{edges} = \\ &= \Delta G_{reaction,terraces} (1 - f_{edges}) + \Delta G_{reaction,edges} f_{edges} \\ &= \Delta G_{reaction,terraces} + f_{edges} (\Delta G_{reaction,edges} - \Delta G_{reaction,terraces}) \end{aligned} \quad (5)$$

where $\Delta G_{reaction,terraces}$ and $\Delta G_{reaction,edges}$ correspond, respectively, to the reaction on terraces and edges, while $f_{terraces}$, f_{edges} denote fractions of these surface sites with their sum equal to unity.

A more detailed analysis is possible; for example, for cubooctahedral shapes of nanoparticles distinguishing reactions on different types of faces

$$\begin{aligned} \Delta G_{reaction} &= \Delta G_{reaction,square_terraces} f_{square_terraces} + \\ &+ \Delta G_{reaction,triangular_terraces} f_{triangular_terraces} + \Delta G_{reaction,edges} f_{edges} \end{aligned} \quad (6)$$

From a relationship between the equilibrium constants and the Gibbs energy of a reaction, it follows for Equation (5)

$$K_{reaction} = e^{-(\Delta G_{reaction,terraces} f_{terraces} + \Delta G_{reaction,edges} f_{edges})/RT} = e^{-(\Delta G_{reaction,terraces} + f_{edges} (\Delta G_{reaction,edges} - \Delta G_{reaction,terraces}))/RT} \quad (7)$$

Or more specifically, for the elementary reaction in Equation (1)

$$K_{reaction} = e^{-\frac{(\Delta G_{A,adsorbed} + \Delta G_{AB,adsorbed} - \Delta G_{B,adsorbed})_{terraces} f_{terraces} + (\Delta G_{A,adsorbed} + \Delta G_{AB,adsorbed} - \Delta G_{B,adsorbed})_{edges} f_{edges}}{RT}} \quad (8)$$

For a slightly more general case, when the Gibbs energy of formation for one of the reactants is not equal to zero, for example, for hydroxylation of an alkane on a metal surface



the Gibbs energy can be calculated from the Gibbs energy of formation of the reactants and products.

$$\Delta G_{reaction} = \Delta G_{ROH} + \Delta G_{catalyst} - \Delta G_{RH} - \Delta G_{O,adsorbed} \quad (10)$$

It should be noted that for a more convenient way of kinetic analysis, the calculations of the Gibbs energy for the catalyst formation (Equation (10) and similar expressions) should be avoided. In the subsequent analysis, the Gibbs energy of adsorption per se will be used without explicitly considering the Gibbs energy for the catalyst

$$\Delta G_{adsorption, O} = \Delta G_{O,adsorbed} - \Delta G_{catalyst} \quad (11)$$

Such an approach gives the following instead of Equation (10)

$$\Delta G_{reaction} = \Delta G_{ROH} - \Delta G_{RH} - \Delta G_{adsorption, O} \quad (12)$$

In Equations (11) and (12), the Gibbs energy of adsorption corresponds to the difference between the Gibbs energy of formation of the adsorbed species on the catalytic sites and the Gibbs energy of formation for the catalyst, per se.

The Gibbs energy for the reaction expressed by Equation (3) is thus

$$\Delta G_{reaction} = \Delta G_{A_2adsorption} - 2\Delta G_{A,adsorption} \quad (13)$$

In a similar fashion, instead of Equation (2)

$$\Delta G_{reaction} = \Delta G_{A,adsorption} + \Delta G_{AB,adsorption} - \Delta G_{B,adsorption} \quad (14)$$

The rate constant of a particular reaction can be expressed, making use of the linear free energy (or Brønsted–Evans–Polanyi) relationship between the reaction constants k and the equilibrium constants K in a series of analogous elementary reactions [11,12]

$$k = g K^\alpha \quad (15)$$

where g and α (Polanyi parameter, $0 < \alpha < 1$) are constants.

More specifically, for the elementary reaction in Equation (1)

$$\begin{aligned} k_{reaction, eq.(1)} &= g e^{-\frac{a[(\Delta G_{A,adsorption} + \Delta G_{AB,adsorption} - \Delta G_{B,adsorption})_{terraces}(1-f_{edges})]}{RT}} * \\ &* e^{-\frac{a[(\Delta G_{A,adsorption} + \Delta G_{AB,adsorption} - \Delta G_{B,adsorption})_{edges} f_{edges}]}{RT}} = \\ &= g e^{-\frac{a[(\Delta G_{A,adsorption} + \Delta G_{AB,adsorption} - \Delta G_{B,adsorption})_{terraces}]}{RT}} * e^{-\frac{a[(\Delta x_A + \Delta x_{AB} - \Delta x_B) f_{edges}]}{RT}} = \\ &= k' e^{-\frac{a[(\Delta x_A + \Delta x_{AB} - \Delta x_B) f_{edges}]}{RT}} \end{aligned} \quad (16)$$

where k' is the cluster size independent rate constant and Δx_A corresponds to differences in Gibbs energy of adsorption on A on terraces and edges, etc.

Similarly, for the reaction given by Equation (9)

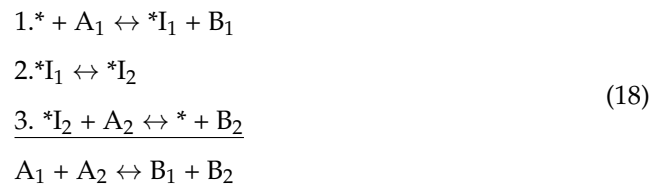
$$k_{reaction, eq.(9)} = g e^{-\frac{a[(\Delta G_{ROH} - \Delta G_{RH})]}{RT}} * e^{-\frac{a[-\Delta G_{adsorption, O}]_{terraces}}{RT}} * e^{-\frac{a[-\Delta x_O] f_{edges}}{RT}} = k' e^{-\frac{a[-\Delta x_O] f_{edges}}{RT}} \quad (17)$$

With Δx_O corresponding to differences in Gibbs energy of oxygen atom adsorption on terraces and edges, etc.

In [7], the fraction of edges was related to the cluster size $f_{edges} \approx 1/d_{cluster}$ when d is in nm, thus allowing the introduction of the cluster size dependence directly into the rate expressions of different types.

3. Christiansen Sequence

As an example of the utilization of the above-described methodology to the derivation of rate equations, two examples will be considered. The first one corresponds to the Christiansen sequence, containing only linear steps [13,14]. The latter implies that, on both sides of an equation of the elementary surface reactions, only one adsorbed species (or vacant sites) is present. The second example treated in the section below addresses a mechanism of ethanol oxidative dehydrogenation with several nonlinear steps. For the Christiansen sequence in Equation (18), the intermediates I_1 and I_2 are generated in subsequent steps 1 and 2, while in the third step the vacant sites $*$ are recovered



For the third step, which is essentially the same as the reaction in Equation (9), the rate expression for the forward and reverse reactions are

$$r_{+3} = k'_{+3} e^{-\frac{a_3(-\Delta x_{I_2})f_{edges}}{RT}} \theta_{I_2} C_{A_2} = \omega_{+3} \theta_{I_2} \quad (19)$$

$$r_{-3} = k'_{-3} e^{-\frac{a_3(\Delta x_{I_2})f_{edges}}{RT}} \theta_V C_{B_2} = \omega_{-3} \theta_V \quad (20)$$

where $\theta_{I_2}; \theta_V$ are the coverage of I_2 and the fraction of vacant sites; C_{A_2} and C_{B_2} are, respectively, concentrations of A_2 and B_2 ; $\omega_{+3}; \omega_{-3}$ are frequencies of step 3 in the forward and reverse directions; and a_3 is the Polanyi parameter of step 3.

The first step of Equation (18) in the forward and reverse directions takes the form

$$r_{+1} = k'_{+1} e^{-\frac{a_1(\Delta x_{I_1})f_{edges}}{RT}} \theta_V C_{A_1} = \omega_{+1} \theta_V \quad (21)$$

$$r_{-1} = k'_{-1} e^{-\frac{a_1(-\Delta x_{I_1})f_{edges}}{RT}} \theta_{I_1} C_{B_1} = \omega_{-1} \theta_{I_1} \quad (22)$$

Finally, for the second step in Equation (18), from a general expression of the Equation (16) type

$$r_{+2} = k'_{+2} e^{-\frac{a_2(\Delta x_{I_2} - \Delta x_{I_1})f_{edges}}{RT}} \theta_{I_1} = \omega_{+2} \theta_{I_1} \quad (23)$$

$$r_{-2} = k'_{-2} e^{-\frac{a_2(\Delta x_{I_1} - \Delta x_{I_2})f_{edges}}{RT}} \theta_{I_2} = \omega_{-2} \theta_{I_2} \quad (24)$$

The overall expression for the three-step Christiansen sequence with linear steps containing the frequencies of steps is derived assuming the steady-state approximation for all intermediates. The detailed derivation is rather tedious, being, however, explained in detail in the literature [10,13]. For the three-step sequence, an expression for TOF takes the following form

$$TOF = \frac{\omega_{+1}\omega_{+2}\omega_{+3} - \omega_{-1}\omega_{-2}\omega_{-3}}{\omega_{+2}\omega_{+3} + \omega_{-3}\omega_{+2} + \omega_{-3}\omega_{-2} + \omega_{+3}\omega_{+1} + \omega_{-1}\omega_{+3} + \omega_{-1}\omega_{-3} + \omega_{+1}\omega_{+2} + \omega_{-2}\omega_{+1} + \omega_{-2}\omega_{-1}} \quad (25)$$

Introducing the frequencies of steps from Equations (19) to (24) into Equation (25) results in

$$TOF = \frac{k'_{+1}k'_{+2}k'_{+3} e^{-\frac{(a_1\Delta x_{I_1} + a_2(\Delta x_{I_2} - \Delta x_{I_1}) + a_3(-\Delta x_{I_2}))f_{edges}}{RT}} C_{A_1} C_{A_2} - k'_{-1}k'_{-2}k'_{-3} e^{-\frac{(a_1(-\Delta x_{I_1}) + a_2(\Delta x_{I_1} - \Delta x_{I_2}) + a_3(\Delta x_{I_2}))f_{edges}}{RT}} C_{B_1} C_{B_2}}{D_{three_step}} \quad (26)$$

where

$$\begin{aligned}
 D_{three_step} = & k'_{+2}k'_{+3}e^{-\frac{a_2(\Delta x_{I_2}-\Delta x_{I_1})+a_3(-\Delta x_{I_2})f_{edges}}{RT}}C_{A_2} + k'_{-3}k'_{+2}e^{-\frac{(a_3(\Delta x_{I_2})+a_2(\Delta x_{I_2}-\Delta x_{I_1}))f_{edges}}{RT}}C_{B_2} + k'_{-3}e^{-\frac{(a_3(\Delta x_{I_2})+a_2(\Delta x_{I_1}-\Delta x_{I_2}))f_{edges}}{RT}}C_{B_2}k'_{-2} + \\
 & + k'_{+1}k'_{+3}e^{-\frac{(a_3(-\Delta x_{I_2})+a_1(\Delta x_{I_1}))f_{edges}}{RT}}C_{A_2}C_{A_1} + k'_{-1}k'_{+3}e^{-\frac{(a_1(-\Delta x_{I_1})+a_3(-\Delta x_{I_2}))f_{edges}}{RT}}C_{B_1}C_{A_2} + k'_{-1}k'_{-3}e^{-\frac{(a_1(-\Delta x_{I_1})+a_3(\Delta x_{I_2}))f_{edges}}{RT}}C_{B_1}C_{B_2} + \\
 & + k'_{+1}k'_{+2}e^{-\frac{(a_1(\Delta x_{I_1})+a_2(\Delta x_{I_2}-\Delta x_{I_1}))f_{edges}}{RT}}C_{A_1} + k'_{-2}k'_{+1}e^{-\frac{(a_2(\Delta x_{I_1}-\Delta x_{I_2})+a_1(\Delta x_{I_1}))f_{edges}}{RT}}C_{A_1} + k'_{-2}k'_{-1}e^{-\frac{(a_2(\Delta x_{I_1}-\Delta x_{I_2})+a_1(-\Delta x_{I_1}))f_{edges}}{RT}}C_{B_1}
 \end{aligned} \quad (27)$$

Some simplifications could be made considering that the value of the Polanyi parameter is equal to 0.5 [10], implying that $\alpha_1 = \alpha_2 = \alpha_3 = \alpha = 0.5$, and introducing the cluster size dependence $f_{edges} \approx 1/d_{cluster}$:

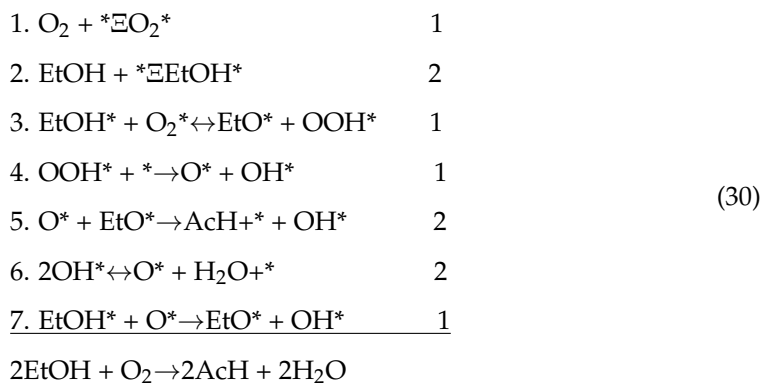
$$TOF = (k'_{+1}k'_{+2}k'_{+3}C_{A_1}C_{A_2} - k'_{-1}k'_{-2}k'_{-3}C_{B_2}C_{B_1})/D'_{three_step} \quad (28)$$

with

$$\begin{aligned}
 D'_{three_step} = & k'_{+2}k'_{+3}e^{-\frac{a(-\Delta x_{I_1})}{RTd_{cl}}}C_{A_2} + k'_{-3}k'_{+2}e^{-\frac{a(2\Delta x_{I_2}-\Delta x_{I_1})}{RTd_{cl}}}C_{B_2} + k'_{-3}e^{-\frac{a\Delta x_{I_1}}{RTd_{cl}}}C_{B_2}k'_{-2} + \\
 & + k'_{+1}k'_{+3}e^{-\frac{a(-\Delta x_{I_2}+\Delta x_{I_1})}{RTd_{cl}}}C_{A_2}C_{A_1} + k'_{-1}k'_{+3}e^{-\frac{a(-\Delta x_{I_1}-\Delta x_{I_2})}{RTd_{cl}}}C_{B_1}C_{A_2} + k'_{-1}k'_{-3}e^{-\frac{a_1(-\Delta x_{I_1}+\Delta x_{I_2})}{RTd_{cl}}}C_{B_1}C_{B_2} + \\
 & + k'_{+1}k'_{+2}e^{-\frac{a\Delta x_{I_2}}{RTd_{cl}}}C_{A_1} + k'_{-2}k'_{+1}e^{-\frac{a(2\Delta x_{I_1}-\Delta x_{I_2})}{RTd_{cl}}}C_{A_1} + k'_{-2}k'_{-1}e^{-\frac{a(-\Delta x_{I_2})}{RTd_{cl}}}C_{B_1}
 \end{aligned} \quad (29)$$

4. Kinetics of Ethanol Oxidation on Gold Catalyst

A kinetic model of ethanol oxidation (EtOH) to acetaldehyde (AcH) over gold catalyst has been proposed recently in the literature [15] based on the following sequence of steps:



In Equation (28), the stoichiometric (Horiuti) numbers of the steps are given. The overall equation corresponds to the sum of all steps multiplied by these numbers.

The model was discussed in [15], invoking DFT calculations and the experimental data. The derivation of the kinetic equation for the mechanism in Equation (28) was presented in detail in the original contribution; therefore, only the cluster size dependence will be considered below. Equation (28) exhibits a combination of reversible (steps 3 and 6), irreversible (steps 4, 5 and 7) and quasi-equilibria steps (steps 1 and 2), making this example very illustrative. The fraction of vacant sites is expressed by

$$\theta_V = \frac{1}{1 + K_2C_{EtOH} + K_1C_{O_2} + \frac{2k_7K_2C_{EtOH}}{k_5} + \frac{k_3k_4K_1C_{O_2}}{k_7(k_4+k_3\frac{k_7}{k_5}C_{EtOH})} + \sqrt{\frac{2}{k_6} \left(\frac{k_3k_4K_1K_2C_{O_2}C_{EtOH}}{k_4+k_3\frac{k_7}{k_5}C_{EtOH}} + \frac{k_6k_3k_4K_1C_{O_2}C_{H_2O}}{k_7(k_4+k_3\frac{k_7}{k_5}C_{EtOH})} \right) + \frac{k_3K_1K_2C_{O_2}C_{EtOH}}{k_4+k_3\frac{k_7}{k_5}C_{EtOH}}} = \frac{1}{D} \quad (31)$$

While the overall rate for acetaldehyde formation $r^{(acetaldehyde)}$ is

$$r^{(acetaldehyde)} = \frac{k_3 k_4 K_1 K_2 C_{O_2} C_{EtOH}}{(k_4 + k_{-3} \frac{k_7}{k_5} C_{EtOH}) D^2} \quad (32)$$

An approach to the derivation of the kinetic equations for such a complex case could be the first to identify the expressions for the Gibbs energy of quasi-equilibria steps, giving in a particular case Equation (28) for the first two steps

$$\Delta G_1 = \Delta G_{O_2,ads,terraces} + f_{edges}(\Delta G_{O_2,ads,edges} - \Delta G_{O_2,ads,terraces}) = \Delta G_{O_2,ads,terraces} + f_{edges}(\Delta x_{O_2,ads}) \quad (33)$$

$$\Delta G_2 = \Delta G_{EtOH,ads,terraces} + f_{edges}(\Delta x_{EtOH,ads}) \quad (34)$$

Subsequently, the equilibrium constants can be described through K_1^t and K_2^t , which correspond to the adsorption constants for the first and second steps on terraces and parameters $\Delta x_{O_2,ads}$, etc., reflecting the difference between the Gibbs energy of dioxygen adsorption on edges and terraces, etc.

$$K_1 = e^{-\Delta G_1/RT} = e^{-\Delta G_{O_2,ads,terraces}/RT} e^{-f_{edges}\Delta x_{O_2,ads}/RT} = K_1^t e^{-\Delta x_{O_2,ads}/RT d_{cl}} \quad (35)$$

$$K_2 = e^{-\Delta G_2/RT} = e^{-\Delta G_{EtOH,ads,terraces}/RT} e^{-f_{edges}\Delta x_{EtOH,ads}/RT} = K_2^t e^{-\Delta x_{EtOH,ads}/RT d_{cl}} \quad (36)$$

For the third step in Equation (28), not containing any species present in the reaction mixture, the Gibbs energy of the surface reaction is

$$\Delta G_3 = \Delta G_{EtO,ads} + \Delta G_{OOH,ads} - \Delta G_{EtOH,ads} - \Delta G_{O_2,ads} = \Delta G_{3,terraces} + f_{edges}(\Delta x_{EtO,ads} + \Delta x_{OOH,ads} - \Delta x_{EtOH,ads} - \Delta x_{O_2,ads}) \quad (37)$$

Analogously, for the fourth and seventh steps

$$\Delta G_4 = \Delta G_{4,terraces} + f_{edges}(\Delta x_{O,ads} + \Delta x_{OH,ads} - \Delta x_{OOH,ads}) \quad (38)$$

$$\Delta G_7 = \Delta G_{7,terraces} + f_{edges}(\Delta x_{EtO,ads} + \Delta x_{OH,ads} - \Delta x_{EtOH,ads} - \Delta x_{O,ads}) \quad (39)$$

Steps 5 and 6 contain reactants, giving

$$\Delta G_5 = \Delta G_{AcH} + \Delta G_{OH,terraces} - \Delta G_{O,terraces} - \Delta G_{EtO,terraces} + f_{edges}(\Delta x_{OH,ads} + \Delta x_{O,ads} - \Delta x_{EtO,ads}) \quad (40)$$

$$\Delta G_6 = \Delta G_{H_2O} + \Delta G_{O,terraces} - 2\Delta G_{OH,terraces} + f_{edges}(\Delta x_{O,ads} - 2\Delta x_{OH,ads}) \quad (41)$$

The rate constants of step 3 in the forward direction is expressed directly from Equation (15)

$$k_3 = g_3 e^{-\alpha_3 \Delta G_{3,terraces}/RT} e^{-\alpha_3 (\Delta x_{EtO,ads} + \Delta x_{OOH,ads} - \Delta x_{EtOH,ads} - \Delta x_{O_2,ads})/RT d_{cl}} \quad (42)$$

Or

$$k_3 = k'_3 e^{-\alpha_3 (\Delta x_{EtO,ads} + \Delta x_{OOH,ads} - \Delta x_{EtOH,ads} - \Delta x_{O_2,ads})/RT d_{cl}} \quad (43)$$

Analogously, for other steps of the similar type

$$k_4 = k'_4 e^{-\alpha_4 (\Delta x_{O,ads} + \Delta x_{OH,ads} - \Delta x_{OOH,ads})/RT d_{cl}} \quad (44)$$

$$k_7 = k'_7 e^{-\alpha_7 (\Delta x_{EtO,ads} + \Delta x_{OH,ads} - \Delta x_{EtOH,ads} - \Delta x_{O,ads})/RT d_{cl}} \quad (45)$$

where

$$k'_3 = g_3 e^{-\alpha_3 \Delta G_{3,terraces}/RT}; k'_4 = g_4 e^{-\alpha_4 \Delta G_{4,terraces}/RT}; k'_7 = g_7 e^{-\alpha_7 \Delta G_{7,terraces}/RT} \quad (46)$$

For steps 5 and 6, in the forward direction

$$k_5 = k'_5 e^{-\alpha_5 (\Delta x_{OH,ads} + \Delta x_{O,ads} - \Delta x_{EtO,ads})/RT d_{cl}} \quad (47)$$

$$k_6 = k'_6 e^{-\alpha_6(\Delta x_{O,ads} - 2\Delta x_{OH,ads})/RTd_{cl}} \quad (48)$$

With

$$k'_5 = g_5 e^{-\alpha_5(\Delta G_{AcH} + \Delta G_{OH,terraces} - \Delta G_{O,terraces} - \Delta G_{EtO,terraces})/RT}; k'_6 = g_6 e^{-\alpha_6(\Delta G_{H_2O} + \Delta G_{O,terraces} - 2\Delta G_{OH,terraces})/RT} \quad (49)$$

The only reversible steps in this reaction mechanism are steps (3) and (6), whose rate constants are apparently

$$k_{-3} = g_3 K_3^{\alpha_3 - 1}; k_{-6} = g_6 K_6^{\alpha_6 - 1} \quad (50)$$

resulting in

$$k_{-3} = g_3 e^{(1-\alpha_3)\Delta G_{3,terraces}/RT} e^{(1-\alpha_3)(\Delta x_{EtO,ads} + \Delta x_{OOH,ads} - \Delta x_{EtOH,ads} - \Delta x_{O_2,ads})/RTd_{cl}} = k'_{-3} e^{(1-\alpha_3)(\Delta x_{EtO,ads} + \Delta x_{OOH,ads} - \Delta x_{EtOH,ads} - \Delta x_{O_2,ads})/RTd_{cl}} \quad (51)$$

$$k_{-6} = g_6 e^{(1-\alpha_6)(\Delta G_{H_2O} + \Delta G_{O,terraces} - 2\Delta G_{OH,terraces})/RT} e^{(1-\alpha_6)(\Delta x_{O,ads} - 2\Delta x_{OH,ads})/RTd_{cl}} = k'_{-6} e^{(1-\alpha_6)(\Delta x_{O,ads} - 2\Delta x_{OH,ads})/RTd_{cl}} \quad (52)$$

With

$$k'_{-3} = g_3 e^{(1-\alpha_3)\Delta G_{3,terraces}/RT}; k'_{-6} = g_6 e^{(1-\alpha_6)(\Delta G_{H_2O} + \Delta G_{O,terraces} - 2\Delta G_{OH,terraces})/RT} \quad (53)$$

Some simplifications are possible if the values of Polanyi parameters are considered to be the same for all steps. Instead of Equation (30), an expression with the cluster size dependence is obtained

$$r^{(acetaldehyde)} = \frac{k'_3 k'_4 K_1^t K_2^t C_{O_2} C_{EtOH} e^{-\alpha(\Delta x_{EtO,ads} - \Delta x_{EtOH,ads} - \Delta x_{O_2,ads} + \Delta x_{O,ads} + \Delta x_{OH,ads}) - (\Delta x_{EtOH,ads} + \Delta x_{O_2,ads})/RTd_{cl}}}{T_0 D^2} \quad (54)$$

where the denominator is also dependent on the cluster size

$$T_0 = k'_4 e^{-\alpha(\Delta x_{O,ads} + \Delta x_{OH,ads} - \Delta x_{OOH,ads})/RTd_{cl}} + k'_{-3} \frac{k'_7}{k'_5} C_{EtOH} e^{\alpha(\Delta x_{EtOH,ads} + 2\Delta x_{O,ads}) + (1-\alpha)(\Delta x_{EtO,ads} + \Delta x_{OOH,ads} - \Delta x_{EtOH,ads} - \Delta x_{O_2,ads})/RTd_{cl}} \quad (55)$$

$$D = 1 + K_2^t e^{-\Delta x_{EtOH,ads}/RTd_{cl}} C_{EtOH} + K_1^t e^{-\Delta x_{O_2,ads}/RTd_{cl}} C_{O_2} + T_1 + T_2 + \sqrt{T_3 + T_4} + T_5 \quad (56)$$

Additionally, the terms in Equation (54) are

$$T_1 = \frac{2k'_7 K_2^t C_{EtOH}}{k'_5} e^{(-2\alpha(\Delta x_{EtO,ads} - \Delta x_{O,ads}) + (\alpha-1)\Delta x_{EtOH,ads})/RTd_{cl}} \quad (57)$$

$$T_2 = \frac{k'_3 k'_4 K_1^t C_{O_2}}{k'_7 T_0} e^{((\alpha-1)\Delta x_{O_2,ads} - 2\alpha\Delta x_{O,ads})/RTd_{cl}} \quad (58)$$

$$T_3 = \frac{2k'_3 e^{/RTd_{cl}} k'_4 K_1^t K_2^t C_{O_2} C_{EtOH}}{k'_6 T_0} e^{((\alpha-1)(\Delta x_{O_2,ads} + \Delta x_{EtOH,ads}) - \alpha(\Delta x_{EtO,ads} + 3\Delta x_{OH,ads}))/RTd_{cl}} \quad (59)$$

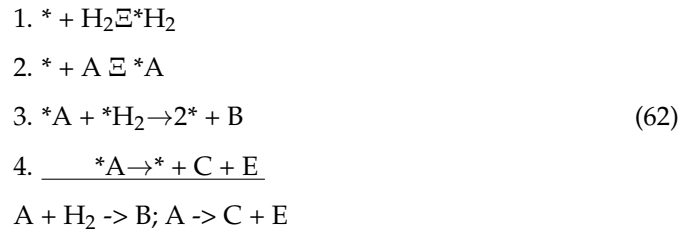
$$T_4 = \frac{2k'_{-6} k'_3 k'_4 K_1^t C_{O_2} C_{H_2O}}{k'_7 k'_6 T_0} e^{((1-2\alpha)\Delta x_{O,ads} - 2\Delta x_{OH,ads} + (\alpha-1)\Delta x_{O_2,ads})/RTd_{cl}} \quad (60)$$

$$T_5 = \frac{k'_3 K_1^t K_2^t C_{O_2} C_{EtOH}}{T_0} e^{(-\alpha(\Delta x_{EtO,ads} + \Delta x_{OOH,ads}) + (\alpha-1)(\Delta x_{O_2,ads} + \Delta x_{EtOH,ads}))/RTd_{cl}} \quad (61)$$

5. Analysis of Selectivity in Parallel Reactions

Apparently, the kinetic expression developed in the previous section is cumbersome, making the analysis of the rate dependence on the cluster size rather challenging. However,

in many cases when kinetics is less complicated, the general methodology described here can be utilized quite easily. As an example, an analysis of a reaction network with two parallel routes with a common adsorption step and mechanistically different rate-determining steps (i.e., mono- and bimolecular) is presented below



This mechanism, which assumes noncompetitive adsorption of hydrogen and the reactant A, was applied in [16] for analysis of the activation energy dependence on the Ru cluster size in furfural (A) hydrogenation to furfuryl alcohol (B) and decarbonylation to furan (C) and CO₂ (E) [17].

For this mechanism, the rate expressions are [16]

$$r_{A \rightarrow B} = \frac{k_{+3}K_1K_2C_A C_{H_2}}{(1 + K_2C_A + K_1C_{H_2})^2} \tag{63}$$

$$r_{A \rightarrow C+E} = \frac{k_{+4}K_2C_A}{1 + K_2C_A + K_1C_{H_2}} \tag{64}$$

Selectivity to furfuryl alcohol is thus

$$\begin{aligned}
 S_{A \rightarrow B} &= \frac{r_{A \rightarrow B}}{r_{A \rightarrow B} + r_{A \rightarrow C+E}} = \frac{\frac{k_{+3}K_1K_2C_A C_{H_2}}{(1+K_2C_A+K_1C_{H_2})^2}}{\frac{k_{+3}K_1K_2C_A C_{H_2}}{(1+K_2C_A+K_1C_{H_2})^2} + \frac{k_{+4}K_2C_A}{1+K_2C_A+K_1C_{H_2}}} = \\
 &= \frac{1}{1 + \frac{k_{+4}(1+K_2C_A+K_1C_{H_2})}{k_{+3}K_1C_{H_2}}}
 \end{aligned} \tag{65}$$

The equilibrium constant of the first step is similar to the one presented above in Equation (33) for oxygen. In the case of hydrogen adsorption, it takes the form

$$K_1 = K_1^t e^{-\Delta x_{H_2,ads}/RTd_{cl}} \tag{66}$$

where $\Delta x_{H_2,ads}$ corresponds to the difference between the Gibbs energy of dihydrogen adsorption on edges and terraces. For the second term, the corresponding constant is apparently

$$K_2 = K_2^t e^{-\Delta x_{A,ads}/RTd_{cl}} \tag{67}$$

From the Gibbs energy for steps 3 and 4, it follows

$$\Delta G_3 = \Delta G_B - \Delta G_{A,ads} - \Delta G_{H_2,ads} = \Delta G_{3,terraces} + f_{edges}(-\Delta x_{A,ads} - \Delta x_{H_2,ads}) \tag{68}$$

$$\Delta G_4 = \Delta G_{3,terraces} + f_{edges}(-\Delta x_{A,ads}) \tag{69}$$

The corresponding rate constants are therefore (with $f_{edges} \approx 1/d_{cl}$, where the cluster size is in nm)

$$k_{+3} = k'_{+3} e^{\alpha_3(\Delta x_{A,ads} + \Delta x_{H_2,ads})/RTd_{cl}}; k_{+4} = k'_{+4} e^{\alpha_4 \Delta x_{A,ads}/RTd_{cl}} \tag{70}$$

resulting subsequently in the expression for the cluster size dependent selectivity

$$S_{A \rightarrow B} = \frac{1}{1 + \frac{k'_{+4}(1+K_2^t e^{-\Delta x_{A,ads}/RTd_{cl}} C_A + K_1^t e^{-\Delta x_{H_2,ads}/RTd_{cl}} C_{H_2}) e^{((\alpha_4 - \alpha_3)\Delta x_{A,ads} + (1 - \alpha_3)\Delta x_{H_2,ads})/RTd_{cl}}}{k'_{+3} K_1^t C_{H_2}}} \quad (71)$$

As demonstrated in [16], if the adsorption terms in the denominators of Equations (61) and (62) are neglected, the dependence of selectivity to the reactants vs. the metal cluster size cannot be correctly accounted for. However, some simplifications of Equation (68) can be performed to make it more tractable. The Polanyi parameters of steps 3 and 4 can be set equal to each and, moreover, equal to 0.5, as often reported in the literature [13]. This leads to the following expression of selectivity

$$S_{A \rightarrow B} = \frac{1}{1 + \frac{k'_{+4}}{k'_{+3} K_1^t C_{H_2}} e^{0.5\Delta x_{H_2,ads}/RTd_{cl}} + \frac{k'_{+4} K_2^t C_A}{k'_{+3} K_1^t C_{H_2}} e^{(0.5\Delta x_{H_2,ads} - \Delta x_{A,ads})/RTd_{cl}} + \frac{k'_{+4}}{k'_{+3}} e^{-0.5\Delta x_{H_2,ads}/RTd_{cl}}} \quad (72)$$

which can describe selectivity in a correct way (Figure 1).

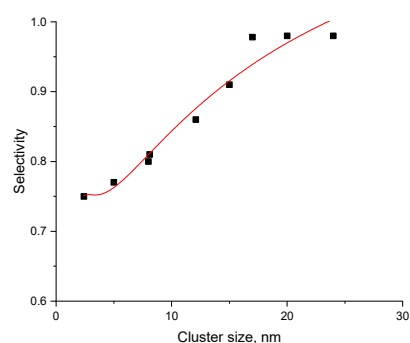


Figure 1. Dependence of selectivity to furfuryl alcohol in transformations of furfural over Ru on silica catalyst at 100 °C. Experimental data digitalized from [17].

Equation (69), although capable of an adequate description of selectivity, is over parametrized because of too many parameters, which correlate with each other. Analysis of the physico-chemical validity of the parameters based on available data cannot be properly performed. Such analysis is in any case outside of the scope of the current work aimed at presenting a general approach for deriving the rate equations of structure-sensitive reactions with arbitrary kinetics.

6. Conclusions

A general methodology for the derivation of kinetic equations in the case of structure-sensitive heterogeneous catalytic reactions was developed following the linear free energy approach for elementary steps. First, the expressions for the Gibbs energy of the elementary steps constituting the mechanism are identified considering the Gibbs energy of adsorption rather than the Gibbs energy of formation for the catalyst and the adsorbed species. This is followed by defining the equilibrium constants of the steps through the respective Gibbs energy. The Gibbs energy of adsorption for surface species is calculated through the contribution of the Gibbs energy on terraces and edges, with the fraction of edges in turn defined as a reciprocal value of the cluster size.

Finally, the rate constants of various steps are expressed as a function of the cluster size with the aid of the linear free energy relationship linking them with the equilibrium constants of the corresponding steps. The resulting rate constants are directly incorporated into the rate equations.

The methodology presented here was illustrated for the three-step generic sequence of all linear steps as well as a multistep mechanism of ethanol oxidative dehydrogenation to acetaldehyde, comprising several linear, nonlinear and quasi-equilibria steps. The resulting

equations can be rather complicated, reflecting, on the other hand, the complexity of the reaction mechanisms. For much simpler cases, like the analysis of selectivity in a parallel reaction of different reaction order, the proposed methodology can be efficiently applied, demonstrating very good correspondence between the experimental data on furfural transformations used as a case study and the calculations.

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