Influence of Structure Sensitivity on Apparent Activation Energy of Parallel Heterogeneous Catalytic Reactions

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Abstract

Analysis of apparent activation energy is presented for different heterogeneous catalytic reactions with parallel reaction routes. In the case of kinetic coupling between catalytic cycles the activation energy in a particular route depends not only on the activation energies of the elementary steps comprising this route, but also on the frequency of the steps in a parallel route. Expressions were derived for coupling between routes through irreversible adsorption of the substrate, quasi-equilibrated binding as well as different substrate adsorption modes. Theoretical analysis of the apparent activation energy was extended for the reaction network with two routes possessing mechanistically different rate determining steps (i.e. monomolecular vs bimolecular). For structure sensitive reactions an expression for the apparent activation energy for parallel reactions was developed for cases with a continuous distribution of active centers and a cubo-octahedral representation of the metal clusters. A comparison between the theoretical analysis and experimental data on transformations of furfural to furfuryl alcohol and furan on ruthenium clusters shows applicability of the developed theoretical framework.

Graphic Abstract

Keywords  Activation energy · Structure sensitivity · Parallel reactions · Furfural · Ruthenium

1 Introduction

Recently there was a renewed interest in a theoretical interpretation of apparent activation energy for a single route multi-step reactions, comprising several elementary steps
The overall rate is then formally expressed using a temperature dependent apparent rate constant

\[ r = k_0 e^{-E_{\text{act}}/RT} C_{\text{sub}}^{m_i}, \]

where \( r \) is the rate, \( C_{\text{sub}}^{m_i} \) is concentration of a substrate \( i \), \( m_i \) — reaction order in this compound, \( E_{\text{act}} \) — apparent activation energy.

In [5] analysis of the apparent activation energy was done for the two step sequence [7, 8] on uniform and nonuniform surfaces [9] as well as for the Langmuir–Hinshelwood mechanism, with the main focus on structure sensitivity [10, 11], e.g. dependence of the rate constants on the cluster size. In [5] theoretical analysis was limited to single route reactions.

For independent reactions the overall (or apparent) activation energy was a subject of theoretical considerations [12–15]. For two first order independent parallel irreversible reactions with the rate constants \( k_{+1} \) and \( k_{+2} \), the overall activation energy \( E_{\text{app}} \) is the weighted sum of the individual ones, that is \( E_{+1} \) and \( E_{+2} \) [12]

\[ E_{\text{app}} = \frac{k_1}{k_{+1} + k_{+2}} E_{+1} + \frac{k_{+2}}{k_{+1} + k_{+2}} E_{+2}. \]

Coupled catalytic cycles were considered in [15] showing that kinetic coupling manifests itself by substantial changes in selectivity. It can be thus hypothesized that in general the activation energy along a particular route can depend on the parallel route as well. In the current work, the main focus was thus on analyzing the apparent activation energy for several reaction mechanisms typical for heterogeneous catalysis, where the parallel routes are coupled in different ways. An emphasis was also put on the dependence of the apparent activation energy on the cluster size.

2 Apparent Activation Energy for a Two-Step Sequence with Both Irreversible Steps

The expression for the apparent (observed) activation energy is given by

\[ E_{\text{act,apparent}} = RT \frac{\partial \ln k_{+1} C_{A_1} k_{+2} C_{A_2}}{\partial T} = RT^2 \frac{\partial}{\partial T} \left( \ln k_{+1} + \ln C_{A_1} + \ln k_{+2} + \ln C_{A_2} - \ln(k_{+1} C_{A_1} + k_{+2} C_{A_2}) \right) \]
Neglecting dependence of the pre-exponential factor on temperature in \( \ln k_{+1} \) in comparison with the exponential term of the Arrhenius equation, it follows for the rate constants that

\[
\frac{\partial}{\partial T} (\ln k_{+1} \exp(-E_{+1}/RT)) = \frac{\partial}{\partial T} (\ln k_{+1} - E_{+1}/RT) = \frac{E_{+1}}{RT^2};
\]

\[
\frac{\partial}{\partial T} (\ln k_{+2} \exp(-E_{+2}/RT)) = \frac{E_{+2}}{RT^2}
\]

(8)

Considering that \( \partial \ln U/\partial T \) for a function \( U \) can be expressed as

\[
\frac{\partial \ln U}{\partial T} = \frac{\partial \ln U}{\partial U} \frac{\partial U}{\partial T} = \frac{1}{U} \frac{\partial U}{\partial T}
\]

(9)

The last term in Eq. (7) is transformed to

\[
\frac{\partial}{\partial T} (\ln(k_{+1} C_{A_1} + k_{+2} C_{A_2})) = \frac{\partial}{\partial T} (\ln k_{+1} C_{A_1} + k_{+2} C_{A_2}) \frac{\partial}{\partial T} (k_{+1} C_{A_1} + k_{+2} C_{A_2})
\]

\[
= \frac{1}{k_{+1} C_{A_1} + k_{+2} C_{A_2}} \frac{\partial}{\partial T} (k_{+1} C_{A_1} + k_{+2} C_{A_2})
\]

\[
= \frac{C_{A_1} k_{+1} e^{-E_{+1}/RT} k_{+1}^2 + C_{A_2} k_{+2} e^{-E_{+2}/RT} k_{+2}^2}{k_{+1} C_{A_1} + k_{+2} C_{A_2}}
\]

\[
= \frac{k_{+1} C_{A_1} + k_{+2} C_{A_2}}{k_{+1} C_{A_1} + k_{+2} C_{A_2}}
\]

(10)

Combining Eqs. (7), (8) and (10) the expression for the apparent activation energy is

\[
E_{\text{app}} = E_{+1} + E_{+2} - \frac{k_{+1} C_{A_1} + k_{+2} C_{A_2}}{k_{+1} C_{A_1} + k_{+2} C_{A_2}} E_{+1} - \frac{k_{+1} C_{A_1} + k_{+2} C_{A_2}}{k_{+1} C_{A_1} + k_{+2} C_{A_2}} E_{+2}
\]

(11)

which can be further modified

\[
E_{\text{app}} = \frac{\omega_{+1}}{\omega_{+1} + \omega_{+2}} E_{+1} + \frac{\omega_{+2}}{\omega_{+1} + \omega_{+2}} E_{+2}
\]

(12)

It follows from Eq. (12) that the apparent activation energy is, as expected, determined by the slowest step. When for example \( \omega_{+1} >> \omega_{+2} \), which in fact depends on the concentration of reactants \( A_1 \) and \( A_2 \), the apparent activation energy is equal to the activation energy of the second step.

The physical meaning of Eq. (12), which was reported in the literature long time ago [1, 16, 17], is that the apparent activation energy of a two-step sequence can be interpreted as an additive value of the activation energies of steps with the weight factors, which are equal to coverages (dimensionless concentrations) of intermediates, including the dimensionless concentration of non-occupied active sites [1].

### 3 Parallel Reactions: Coupling Between Cycles

In the current work we would like to extend the treatment of activation energy for parallel reactions to cases when there is kinetic coupling between catalytic cycles. This implies that when two catalytic reactions are taking place simultaneously, their individual rates are not the same when they are run separately with the same catalyst under the same conditions. The reason for such behavior is that reactants and products in each reaction compete for the same catalytic sites [18, 19]. The simple catalytic cycle shown in Fig. 2 and Eq. (13) describes the kinetically important steps for parallel reactions giving two products B and C.

1. \( Z + A \rightarrow ZI \)
2. \( ZI + D_2 \rightarrow Z + B + W \)
3. \( ZI + D_2 \rightarrow Z + C + W \)

(13)

where \( D_2 \) is a reactant (e.g. dihydrogen or dioxygen), B and C are products, W is also a (optional) product (e.g. water in an oxidation reaction). For the sake of clarity assuming that all steps are irreversible, the rate of formation the product B can be easily expressed

\[
r_B = \frac{k_{+1} C_{A_1} k_{+2} C_{D_2}}{k_{+1} C_{A_1} + k_{+2} C_{D_2} + k_{+3} C_{D_2}}
\]

(14)

or

\[
r_B = \frac{\omega_{+1} \omega_{+2}}{\omega_{+1} + \omega_{+2} + \omega_{+3}}
\]

(15)

Analogously for the generation of product C

\[
r_C = \frac{k_{+1} C_{A_1} k_{+3} C_{D_2}}{k_{+1} C_{A_1} + k_{+2} C_{D_2} + k_{+3} C_{D_2}} = \frac{\omega_{+1} \omega_{+3}}{\omega_{+1} + \omega_{+2} + \omega_{+3}}
\]

(16)

The overall rate is

\[
r_A = \frac{\omega_{+1} \omega_{+2} + \omega_{+3}}{\omega_{+1} + \omega_{+2} + \omega_{+3}}
\]

(17)

![Fig. 2 Kinetic coupling between cycles with a single intermediate](image-url)
The apparent activation energy for the reaction rate in Eq. (17) is

\[ E_{a,\text{app}} = E_{+1} + \frac{\omega_{+2}}{\omega_{+2} + \omega_{+3}} E_{+2} + \frac{\omega_{+3}}{\omega_{+2} + \omega_{+3}} E_{+3} - \frac{\omega_{+1}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} E_{+1} - \frac{\omega_{+2}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} E_{+2} - \frac{\omega_{+3}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} E_{+3} \]  

or

\[ E_{a,\text{app}} = \frac{\omega_{+2} + \omega_{+3}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} E_{+1} + \frac{\omega_{+1} \omega_{+2}}{(\omega_{+2} + \omega_{+3})(\omega_{+1} + \omega_{+2} + \omega_{+3})} E_{+2} + \frac{\omega_{+1} \omega_{+3}}{(\omega_{+2} + \omega_{+3})(\omega_{+1} + \omega_{+2} + \omega_{+3})} E_{+3}. \]

For the rates along the reaction routes the apparent activation energies are respectively

\[ E_{a,\text{app,B}} = E_{+1} + E_{+2} - \frac{\omega_{+1}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} E_{+1} - \frac{\omega_{+2}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} E_{+2} = \frac{\omega_{+2} + \omega_{+3}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} E_{+1} + \frac{\omega_{+1} + \omega_{+3}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} E_{+2} \]

\[ E_{a,\text{app,C}} = \frac{\omega_{+3}}{\omega_{+2} + \omega_{+3}} E_{+2} + \frac{\omega_{+1} + \omega_{+2}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} E_{+3}. \]

Equations (20) and (21) illustrate coupling between the cycles, when the activation energy in a particular route depends not only on the activation energies of the elementary steps comprising this route, but also on the frequency of the step in another route or in other words contributions of a parallel route.

To highlight this point let us assume that the first step in Eq. (13) is the rate limiting. By considering that \( \omega_{+1} \) is low, instead of Eqs. (20) and (21) one gets

\[ E_{a,\text{app,B}} = E_{+1} + \frac{\omega_{+3}}{\omega_{+2} + \omega_{+3}} E_{+2} \]

and

\[ E_{a,\text{app,C}} = E_{+1} + \frac{\omega_{+2}}{\omega_{+2} + \omega_{+3}} E_{+3}. \]

Clearly if there is only one route (i.e. \( \omega_{+1} = 0 \)) the apparent activation energy for the first route (formation of B) with the first step in Eq. (13) being the rate limiting, is just the activation energy of that step.

Otherwise, the value of activation energy depends on the relative contribution of the competing route, which is different from what follows from the consideration for independent routes [12].

In a more general case, the ratio of activation energies for two products is expressed by

\[ E_{a,\text{app,B}} = \frac{E_{+1}(\omega_{+2} + \omega_{+3}) + E_{+2}(\omega_{+1} + \omega_{+3})}{E_{+1}(\omega_{+2} + \omega_{+3}) + E_{+3}(\omega_{+1} + \omega_{+2})}. \]

4 Parallel Reactions: Different Adsorption Modes/Reactions of Mixtures

In the previous section the (surface) intermediate \( I \) was considered to be the same (Eq. 13) in two routes leading to different products. In a more general case, the starting compound can adsorb on the surface in different adsorption modes [20]. As an example a mechanism of hydrogenation of a compound with two functional groups (i.e. an unsaturated aldehyde) can be envisaged:

1. \( Z + A \to ZI_1 \)
2. \( ZI_1 + H_2 \to Z + B \)
3. \( Z + A \to ZI_2 \)
4. \( ZI_2 + H_2 \to Z + C \)

\[ A + H_2 \to B; \quad A + H_2 \to C \]

The final chemical equations are the same as for Eq. (13) with the only difference that in mechanism (25) there are two surface intermediates \( ZI_1 \) and \( ZI_2 \).

The rate equations for two reaction routes in Eq. (25) can be easily derived following the basic principles of derivation of reaction rate equations [21]

\[ r_B = \frac{k_+ C_A k_{+2} C_{H_2}}{k_+ C_A + k_{+2} C_{H_2} + k_{+3} C_A + k_{+4} C_{H_2}}, \]

\[ r_C = \frac{k_+ C_A k_{+3} C_A}{k_+ C_A + k_{+3} C_A + k_{+4} C_{H_2}}. \]
\[ r_C = \frac{k_{+3}CA_k_{+4}CH_2}{k_{+1}CA + k_{+2}C_H2 + k_{+3}CA + k_{+4}C_H2}. \]  
\text{(27)}

Or respectively

\[ r_B = \frac{\omega_{+1}\omega_{+2}}{\omega_{+1} + \omega_{+2} + \omega_{+3} + \omega_{+4}} \]  
\text{(28)}

and

\[ r_C = \frac{\omega_{+3}\omega_{+4}}{\omega_{+1} + \omega_{+2} + \omega_{+3} + \omega_{+4}} \]  
\text{(29)}

General forms of Eqs. (28) and (29) can be applied obviously not only for hydrogenation reactions, but, for example parallel isomerization reactions

1. \( Z + A \rightarrow ZI_1 \)
2. \( ZI_1 + H_2 \rightarrow Z + B \)
3. \( Z + A \rightarrow ZI_2 \)
4. \( ZI_2 + H_2 \rightarrow Z + C \)

\( A > B; \ A \rightarrow C \)

\text{(30)}

To make the analysis of the apparent activation energy more straightforward instead of Eq. (25) the mechanism with quasi-equilibrated binding (adsorption) of reactants to the surface sites can be considered

1. \( Z + A \approx ZI_1 \)
2. \( ZI_1 + H_2 \rightarrow Z + B \)
3. \( Z + A \approx ZI_2 \)
4. \( ZI_2 + H_2 \rightarrow Z + C \)

\text{(32)}

The reaction rates for two routes in Eq. (32) can be written in a straightforward way

\[ r_B = \frac{K_1 C_A k_{+2} C_H2 e^{(-\Delta H_1 - E_{+2})/RT}}{1 + K_1 C_A e^{-\Delta H_1/RT} + K_3 C_A e^{-\Delta H_3/RT}} \]  
\text{(33)}

\[ r_C = \frac{K_3 C_A k_{+4} C_H2 e^{(-\Delta H_3 - E_{+4})/RT}}{1 + K_1 C_A e^{-\Delta H_1/RT} + K_3 C_A e^{-\Delta H_3/RT}}. \]  
\text{(34)}

where \( \Delta H < 0 \), when adsorption is exothermal. The apparent activation energies along different reaction routes are

\[ E_{\text{apparent}, B} = RT^2 \frac{\partial \ln \frac{K_1 C_A k_{+2} C_H2 e^{(-\Delta H_1 - E_{+2})/RT}}{1 + K_1 C_A e^{-\Delta H_1/RT} + K_3 C_A e^{-\Delta H_3/RT}}}{\partial T} = E_{+2} + \frac{\Delta H_1}{1 + K_1 C_A + K_3 C_A}, \]  
\text{(35)}

\[ E_{\text{apparent}, C} = RT^2 \frac{\partial \ln \frac{K_3 C_A k_{+4} C_H2 e^{(-\Delta H_3 - E_{+4})/RT}}{1 + K_1 C_A e^{-\Delta H_1/RT} + K_3 C_A e^{-\Delta H_3/RT}}}{\partial T} = E_{+4} + \frac{\Delta H_3}{1 + K_1 C_A + K_3 C_A}. \]  
\text{(36)}

where \( A \) stands for a substrate, \( B \) and \( C \) for its isomers. Expressions for the frequency of step should be just modified (e.g. \( \omega_{+4} = k_{+4} \)).

Moreover, for other reactions networks, e.g. hydrogenation of a mixture of two compounds \( A_1 \) and \( A_2 \)

1. \( Z + A_1 \rightarrow ZI_1 \)
2. \( ZI_1 + H_2 \rightarrow Z + B \)
3. \( Z + A_2 \rightarrow ZI_2 \)
4. \( ZI_2 + H_2 \rightarrow Z + C \)

\( A_1 + H_2 \rightarrow B; \ A_2 + H_2 \rightarrow C \)

\text{(31)}

the reaction rates are expressed by Eqs. (28) and (29) with \( \omega_{+1} = k_{+1} C_{A_1} \) and \( \omega_{+3} = k_{+3} C_{A_2} \).

If compound \( A \) is attached to the surface in the same adsorption mode

1. \( Z + A \approx ZI \)
2. \( ZI + H_2 \rightarrow Z + B \)
3. \( ZI + H_2 \rightarrow Z + C \)

\( A + H_2 \rightarrow B; \ A + H_2 \rightarrow C \)

\text{(37)}

the apparent activation energies along different reaction routes take the form

\[ E_{\text{apparent}, B} = E_{+2} + \frac{\Delta H_1}{1 + K_1 C_A}, \]  
\text{(38)}
The overall activation energy for the mechanism expressed in Eq. (37) takes the form

\[ E_{a,\text{app}} = \frac{k_0^e e^{-(E_z/RT) (E_{z_2} + \Delta E_2)}}{k_{+2}^e e^{-(E_{z_1}/RT) (E_{z_3} + \Delta E_1)}} \]

Clearly showing a more complex dependence than what would be expected from independent first order reactions, that is the one given by Eq. (1).

5 Cluster Size Dependence of Apparent Activation Energy

Different approaches were proposed in the literature to account for the dependence of reaction rate (or turnover frequency) on the metal cluster size [22–24]. In the model which assumes a difference between Gibbs energy of adsorption on edges and terraces:

\[ \chi = \frac{(\Delta G_{\text{ads,edges}} - \Delta G_{\text{ads,terraces}})}{RT} \]

and the ratio between the surface to total sites inversely proportional to the cluster size [22], the rate constants for adsorption (e.g. \( Z + A \rightarrow ZI \)) or alternatively desorption or surface reaction steps with desorption (\( ZI + H_2 \rightarrow Z + B \)) are respectively expressed

\[ k_{\text{ads}} = k_{0,\text{ads}} e^{-\alpha \chi/d_{\text{cluster}}} \] \hspace{1cm} (42)

\[ k_{\text{des}} = k_{0,\text{des}} e^{(1-\alpha) \chi/d_{\text{cluster}}} \] \hspace{1cm} (43)

where \( \alpha \) is the Polanyi parameter and \( d_{\text{cluster}} \) is given in nm. For quasi-equilibrium adsorption from Eqs. (42) and (43) one easily gets

\[ K_{\text{ads}} = K_{0,\text{ads}} e^{-x/d_{\text{cluster}}} \]

Obviously when the cluster size is increasing, the limiting value of the rate constants and adsorption coefficients correspond to respectively reaction and adsorption on large extended surfaces /terraces.

Let us analyze one example from the mechanisms addressed above. For the sake of generality instead of mechanism (37) it is worth to analyze a reaction network with two parallel routes with a common adsorption step and mechanistically different rate determining steps (i.e. monomolecular)

1. \( Z + H_2 \rightarrow ZH_2 \)
2. \( Z + A \rightarrow ZI \)
3. \( ZI + H_2 \rightarrow 2Z + B \)
4. \( ZI \rightarrow Z + C + D \)

\[ A + H_2 \rightarrow B; \ A \rightarrow C + D \]

The mechanism assumes competitive adsorption of hydrogen and can be used for example for analysis of Ru catalysed furfural transformations resulting in hydrogenation to furfuryl alcohol and decarbonylation to furan and \( CO_2 \) [25].

The rate expressions can be easily derived for hydrogenation

\[ r_{A \rightarrow B} = \frac{k_{+3} K_1 K_2 C_A C_{H_2}}{(1 + K_2 C_A + K_1 C_{H_2})^2} \] \hspace{1cm} (46)

and decarbonylation

\[ r_{A \rightarrow C + D} = \frac{k_{+4} K_2 C_A}{1 + K_2 C_A + K_1 C_{H_2}} \] \hspace{1cm} (47)

These rate expressions can be rewritten [5] considering the temperature dependence

\[ r_{A \rightarrow B} = \frac{k_{+3} K_1 K_2 C_A C_{H_2} e^{-\Delta G_{\text{ads,edges}}/RT - \Delta G_{\text{ads,terraces}}/RT - \Delta G_{\text{cluster}}/RT - E_z + \Delta H_z}}{{(1 + K_1 e^{-(\Delta G_{\text{ads,edges}}/RT - \Delta G_{\text{ads,terraces}}/RT - \Delta G_{\text{cluster}}/RT - E_z + \Delta H_z)} C_{H_2} + K_{+2} e^{-(\Delta G_{\text{ads,edges}}/RT - \Delta G_{\text{ads,terraces}}/RT - \Delta G_{\text{cluster}}/RT - E_z + \Delta H_z)} C_A))}^2} \]

\[ r_{A \rightarrow C + D} = \frac{k_{+4} K_2 C_A e^{-\Delta G_{\text{ads,edges}}/RT - \Delta G_{\text{ads,terraces}}/RT - \Delta G_{\text{cluster}}/RT - E_z + \Delta H_z}}{{(1 + K_1 e^{-(\Delta G_{\text{ads,edges}}/RT - \Delta G_{\text{ads,terraces}}/RT - \Delta G_{\text{cluster}}/RT - E_z + \Delta H_z)} C_{H_2} + K_{+2} e^{-(\Delta G_{\text{ads,edges}}/RT - \Delta G_{\text{ads,terraces}}/RT - \Delta G_{\text{cluster}}/RT - E_z + \Delta H_z)} C_A))} \]

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where $K_{1,0}$ is the pre-factor for adsorption of hydrogen, etc., $k_{+3,0}$ is the pre-factor for the rate constant of the step 3, etc. $\alpha_2$ is the Polanyi parameter of this step, $\Delta G_{\text{ads,edges}}$, $\Delta G_{\text{ads,terraces}}$, $\Delta H_A$ correspond respectively to the Gibbs energy of adsorption of compound A on edges and terraces and to the heat of adsorption on terraces [5]. The expressions for apparent activation energies along two routes as a function of the metal cluster size are rather complex

\[
E_{\text{act,apparent,B}} = E_{+2} + \Delta H_{H_2} + \alpha_2(\Delta \Delta G_{\text{ads,H}_2})/d_{\text{cluster}} + \Delta H_A + \alpha_4(\Delta \Delta G_{\text{ads,A}})/d_{\text{cluster}} \left(1 + K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2} + K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A\right)^2,
\]

\[
E_{\text{act,apparent,C+D}} = E_{+4} + \Delta H_A + \alpha_4(\Delta \Delta G_{\text{ads,A}})/d_{\text{cluster}} \left(1 + K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2} + K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A\right)^2 \cdot
\]

\[
\frac{K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2} + K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A}{1 + K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2} + K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A}
\]

where $\Delta \Delta G_{\text{ads,A}}$ is the difference between Gibbs energy of adsorption on edges and terraces of compound A and $L$ is defined as

\[
L = K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2} + K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A \cdot
\]

\[
+ 2K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2}K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A \cdot
\]

\[
+ 2K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2}^2 + 2K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A^2 \cdot
\]

\[
E_{\text{act,apparent,C+D}} = E_{+4} + \Delta H_A + \alpha_4(\Delta \Delta G_{\text{ads,A}})/d_{\text{cluster}} \left(1 + K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2} + K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A\right)^2 \cdot
\]

\[
\frac{K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2} + K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A}{1 + K_{1,0}e^{-\Delta \Delta G_{\text{ads,H}_2}/RT}/C_{H_2} + K_{2,0}e^{-\Delta \Delta G_{\text{ads,A}}/RT}/C_A}
\]

Equations (50)–(52) are rather cumbersome to analyse dependences of activation energy on the cluster size. For a particular case of furfural hydrogenation to furfuryl alcohol and decarbonylation to furan and CO$_2$ [25] exhibiting the first order dependence in the substrate in both reactions and the first order in hydrogen for the hydrogenation reactions, expressions for the rates and activation energy can be substantially simplified.
\[ r_{A \rightarrow B} = k_{A \rightarrow B} C_A C_H e^{-\frac{\Delta H_{A}^{-} + \Delta H_{B}^{+}}{RT}}, \]
\[ r_{A \rightarrow C+D} = k_{A \rightarrow C+D} C_A e^{-\frac{\Delta H_{A}^{-} + \Delta H_{C+D}^{+}}{RT}}, \]
\[ E_{\text{act,apparent},B} = E_{B} + \Delta H_{B} + a_{3}(\Delta \Delta G_{\text{ads},A})/d_{\text{cluster}} \]
\[ + \Delta H_{A} + a_{4}(\Delta \Delta G_{\text{ads},A})/d_{\text{cluster}}, \]
\[ E_{\text{act,apparent},C+D} = E_{C+D} + \Delta H_{A} + a_{4}(\Delta \Delta G_{\text{ads},A})/d_{\text{cluster}} \]

For the sake of simplicity in what follows a cuboctahedron model [26] will be considered assuming also that activity of atoms in corners and edges is the same. The fraction of terraces can be calculated as

\[ f_{\text{terrace,cuboctahedra}} = \frac{n_{\text{atoms,terrace}}}{n_{\text{all,surface,atoms}}} \]
\[ = \frac{8(3m^2 - 9m + 7)^2 + 6(m - 2)^2}{30m^2 - 60m + 32}, \]

where \( m \) is related to the cluster size and the atom diameter

\[ m = \frac{d_{\text{cluster}}}{2d_{\text{at}}}. \]

The experimental data in [25] correspond to the first order dependence in the substrate concentration along both pathways and the first order in hydrogen pressure for hydrogenation. It is, however, instructive to analyze an expression for the apparent activation energy in the case of an Eley–Rideal reaction mechanism, where the apparent turnover frequency is defined through respective contributions on terraces and edges

\[ k_{\text{app,TOF}}e^{-E_{\text{app,TOF}}/RT} = k_0 e^{-E_{\infty,\infty}/RT} \frac{K_A e^{-\Delta H_A}/RT C_A}{1 + K_L e^{-\Delta H_L}/RT C_A} f_{\text{terrace}} + k_0 e^{-E_{\infty,\infty}/RT} K_e e^{-\Delta H_e}/RT C_A (1 - f_{\text{terrace}}) \]

An expression for the apparent activation energy can be derived using the same approach as discussed above giving

\[ \text{TOF} = \text{TOF}_{\text{terrace}}f_{\text{terrace}} + \text{TOF}_{\text{edges}}f_{\text{edges}} + \text{TOF}_{\text{corners}}f_{\text{corners}} \]

\[ \text{Fig.} 4 \quad \text{Influence of the particle size on productivity and apparent activation energy for furfural hydrogenation to furfuryl alcohol and decarboxylation of furan. Comparison between experimental data (taken from [25] at 10 bar of hydrogen and 100–165 °C for silica supported Ru catalysts) and calculations according to Eqs. (62)–(64).} \]
The last term in Eq. (61) is independent on the cluster size. For the case of the first order reaction in the substrate in the context of decarbonylation of furfural, Eq. (60) takes the form

$$\begin{align*} E_a &= k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_{a,4} + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) \quad \text{after terraces} \\
&+ k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) \\
&- 1 + K^4 e^{-\Delta H_{a,4}/RT} C_A + K^4 e^{-\Delta H_{a,4}/RT} C_A + K^4 e^{-\Delta H_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A^2. \end{align*}$$

(61)

6 Conclusions

Expressions for apparent activation energy along parallel routes were derived for several heterogeneous catalytic reactions with coupling between the reaction routes. For independent parallel reactions the overall apparent activation energy depends on the kinetic parameters of individual paths, however, the activation energies along different routes do not depend on each other. In the case of kinetic coupling between catalytic cycles the activation energy along a particular path depends not only on the activation energies of the elementary steps comprising this route, but also on the kinetic parameters of a parallel route. Expressions for the apparent activation energies were derived for mechanisms with coupling between routes through irreversible adsorption of the substrate, quasi-equilibrated binding as well as substrate adsorption with different adsorption modes. In this way, catalytic cycles with a common intermediate and with or without a common step were considered. Expressions for the apparent activation energy show a more complex

$$\begin{align*} k_{app, TOF} e^{-E_{app, TOF}/RT} &= k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_{a,4} + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) \\
&+ k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) \\
&- 1 + K^4 e^{-\Delta H_{a,4}/RT} C_A + K^4 e^{-\Delta H_{a,4}/RT} C_A + K^4 e^{-\Delta H_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A^2. \end{align*}$$

(62)

resulting in

$$\begin{align*} E_{app} &= \frac{k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_{a,4} + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) - 1 + K^4 e^{-\Delta H_{a,4}/RT} C_A + K^4 e^{-\Delta H_{a,4}/RT} C_A + K^4 e^{-\Delta H_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A^2}{k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A} \quad \text{after terraces}. \end{align*}$$

(63)

In a similar way for the hydrogenation route the activation energy is

$$\begin{align*} E_3 &= \frac{k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_{a,4} + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A(E_{a,4} + \Delta H_a + \Delta H_a) - 1 + K^4 e^{-\Delta H_{a,4}/RT} C_A + K^4 e^{-\Delta H_{a,4}/RT} C_A + K^4 e^{-\Delta H_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A^2}{k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A + k^4 e^{-E_{a,4}/RT} K^4 e^{-\Delta H_{a,4}/RT} C_A} \quad \text{after terraces}. \end{align*}$$

(64)

A comparison between calculations and theoretical predictions for the catalytic activity, which is independent on the reaction mechanism, using Eq. (57) and assuming that edges and corners behave in the same way, is shown in Fig. 4a. Figure 4b displays the calculation results for the apparent activation energy [Eqs. (63) and (64)] along two routes using a generic expression

$$\begin{align*} E_{app} &= a_1 E_{app}(1 - f_{terraces}) + a_2 E_{app}(1 - f_{terraces}) \quad \text{after terraces} \\
&+ a_3 E_{app}(1 - f_{terraces}) \quad \text{after terraces}. \end{align*}$$

(65)

It is clear from Fig. 4b that in general the model is able to capture the cluster size dependence of the activation energy using a simple cubo-octahedron representation of metal clusters.
dependence on the activation energy of steps than what would be expected from independent first order reactions, comprising also the heats of adsorption.

Theoretical analysis of the apparent activation energy was extended for the reaction network with two routes, when they have mechanistically different rate determining steps (i.e. monomolecular vs bimolecular reactions).

Analysis of the cluster size dependence of the apparent activation energy for parallel reactions was developed considering two models. The first assumes a continuous distribution of Gibbs energy of adsorption on active centers and an inverse dependence of the cluster size on the ratio between the surface to total sites. This model accounts for structure sensitivity by incorporating the cluster size dependence in the rate constants. An alternative model does not explicitly consider the reaction mechanism and describes turnover frequency through relative contributions of TOF on edges, corners and terraces. A cubo-octahedral representation of the metal clusters was selected in this work.

A comparison between the theoretical analysis and experimental data on hydrogenation of furfural to furfuryl alcohol and decarbonylation to furan on ruthenium clusters shows applicability of the latter theoretical framework to describe the apparent activation energy along these parallel pathways.

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Compliance with Ethical Standards

Conflict of interest The author declares no conflict of interest.

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