Structure insensitivity: application of the surface electronic gas model

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Structure sensitive and insensitive reactions with nonuniformly reactive adsorbates are discussed in terms of the surface electronic gas model using the Polanyi parameter (α). For the liquid-phase hydrogenation it was demonstrated, that the reaction is structure insensitive when α is equal to unity, which in terms of the surface electronic gas model means that effective charges of adsorbed species and activated complexes in transition state are equal.

Keywords: Structure insensitivity; surface electronic gas model

1. Introduction

The theory of the reaction kinetics of heterogeneous catalysis is an important branch of the science of catalysis, which has also practical applications in process optimization and reactor design. In recent years new concepts based on surface science of single crystal surfaces, such as for example surface reconstruction and ordered overlayers, were introduced. It was also shown that adsorbate–adsorbate interactions play important roles in catalysis. Such results have given the possibility to develop microkinetic models based on reaction rate constants and binding energies deduced from surface science experiments [1–3].

One of the questions in the theory of heterogeneous kinetics which attracted attention of several research groups is the problem of structure insensitive reactions [4], when reaction rate is independent of the particle size. As it is pointed out in ref. [5] in several cases, for example catalytic hydrogenation of olefins, independence of particle size over supported catalysts correlates with the independence of the surface plane in single-crystal catalysts. However, not only on polycrystalline surfaces but also on single-crystal faces isosteric heat of adsorption depends on the coverage [3,5], thus indicating nonuniform behaviour of adsorbed species as a function of conversion.

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A question which arises can be formulated in the following way: why is a surface, which thermodynamically acts nonuniformly, kinetically insensitive to particle size and in catalytic kinetic modelling can classical kinetics be successfully applied [3,4]. A semiempirical Polanyi relation [6] can be considered as a bridge between thermodynamics and kinetics, and below we will discuss some aspects of structure insensitive reactions using the Polanyi relation. Due to some confusion which exists in literature, in the following discussion the definitions used in ref. [7] will be applied.

2. Models of adsorbed layers

One of the simplest physical models which is used in catalytic kinetics is the model of ideal adsorbed layers. In this case all surface sites are considered as identical and the interactions between adsorbed particles are neglected. Such surface was defined as uniform. However, this model of an ideal adsorbed layer disagrees with a number of experimental data. For example differential heat of adsorption is not constant as a rule but decreases with surface coverage, and, correspondingly, rate of adsorption and adsorption equilibrium cannot be described by the Langmuir equation of Langmuir isotherm. In several cases the kinetics of catalytic reactions disagrees with the equations obtained on the basis of the model of ideal adsorbed layers. For example, the kinetics of ammonia synthesis obeys the well-known Temkin–Pyzhev equation, which was explained in terms of nonuniform surface [7]. Ammonia synthesis is also an example of a structure sensitive reaction [8].

Two different assumptions are generally used for the description of the physical chemistry of real adsorbed layers: either surface sites are different or there is mutual influence of adsorbed species. According to ref. [7] the first case is defined as biographical nonuniformity and the second one as induced nonuniformity. On biographical nonuniform surfaces a certain distribution of properties is considered. Such nonuniformity can be either chaotic, when the adsorption energy on a given site is independent of the neighbor site or discrete. However, if in an elementary surface reaction only one adsorbed particle is involved the difference in these distributions cannot be observed [9]. Different functions determining the fraction of the total number of surface sites characterized by definite adsorption energy of a given substance were proposed and one, which accounts to the Temkin adsorption isotherm, corresponds even to nonuniform surfaces [7]. However, there are no physical reasons for such distribution [10], and, as it was pointed out, isosteric heat of adsorption is dependent on coverage also on single crystals and such dependence corresponds to the Temkin isotherm.

In order to describe such data another type of model can be used – induced nonuniformity. (We have to note that sometimes in literature what is defined in ref. [7] as induced nonuniformity, is discussed as a uniform surface with binding

energies of adsorbed particles varying with coverage due to adsorbate–adsorbate interactions.) Effects of adsorbate–adsorbate interactions are often described using the lattice gas model. In such a model each adsorbate is assumed to be localized on a two-dimensional array of surface sites, and each site is assumed to be either vacant or occupied by a single adsorbate. A given adsorbate can interact with adsorbates on nearest-neighbor sites, next-nearest sites, etc., but in most variants of the lattice gas model only nearest-neighbor interactions are taken into account. One of the more widely used postulates is the quasi-chemical approximation which assumes that the adsorbates maintain an equilibrium distribution on the surface. Even in this case the equations for the reaction rates are extremely complicated [11]; therefore there are some limitations in their application in the description of kinetics of heterogeneous catalytic reactions, especially when reaction is complex. Another model, which corresponds to induced nonuniformity was developed in refs. [9,12,13]: the model of surface electronic gas. This model is based on the assumption that chemisorbed particles feed their electrons into the surface layer of the solid or take electrons from it, forming at the surface a kind of two-dimensional electronic gas. The changes in electron concentration in the solid proceed only in the subsurface layer. The model can be used only when surface coverage is not small. The specific feature of the model is the assumption that the energy of the adsorbed layer is a function only of the total number of adsorbed species and does not depend on their arrangement. This model will be further used for the discussion of structure insensitive reactions.

3. Polanyi relation

This relation corresponds to a linear relationship between the Gibbs activation energy and the standard change of the Gibbs energy. If the standard entropy of each kind of adsorbed species and activated complexes in the case of nonuniformly reactive adsorbates does not differ substantially, this relation is equivalent to the linear dependence between the variation of internal energy change and activation energy [7].

4. Ichikawa considerations [14,15]

Recently [14], an attempt was made in the interpretation of volcano curves, structure sensitivity and insensitivity in the reactions with nonuniformly reactive adsorbates using the Polanyi relation. Due to the fact that variation of properties on nonuniform surfaces (discrete biographical nonuniformity and induced nonuniformity) can be presented as a function of coverage, in refs. [14,15] nonuniformity was considered in general and the type of nonuniformity was not specified. The analysis was done in ref. [14] using a two-step mechanism [16,17],

1. $A + Z = ZI + C$
2. $B + ZI = Z + D$

$$A + B = C + D, \tag{I}$$

where A, B are reactants, C and D are products, Z is the surface site and I is an adsorbed intermediate. The reaction rate with nonuniformly reactive adsorbates was described in refs. [14,15] as follows:

$$r = S(\theta)\frac{k_1^0 P_A k_2^0 P_B - k_{-1}^0 P_C k_{-2}^0 P_D}{k_1^0 P_A + k_1^0 P_B + k_{-1}^0 P_C + k_{-2}^0 P_D}, \tag{1}$$

where k_i^0 are the rate constants corresponding to systems with uniformly reactive adsorbates, θ is the surface coverage by I and the function $S(\theta)$ represents the nonuniform character of the system with nonuniformly reactive adsorbates. Eq. (1) was used in refs. [14,15] for the explanation of structure insensitivity in heterogeneous catalytic reactions. In order to deduce eq. (1) in ref. [14] firstly the following equation for the reaction rate was proposed:

$$r = \frac{k_1 P_A k_2 P_B - k_{-1} P_C k_{-2} P_D}{k_1 P_A + k_2 P_B + k_{-1} P_C + k_{-2} P_D}, \tag{2}$$

where k are the rate constants:

$$k_1 = k_1^0 \exp(-\alpha_1 \beta\theta),$$

$$k_2 = k_2^0 \exp[(1 - \alpha_2)\beta\theta],$$

$$k_{-1} = k_{-1}^0 \exp[(1 - \alpha_1)\beta\theta],$$

$$k_{-2} = k_{-2}^0 \exp(-\alpha_2 \beta\theta). \tag{3}$$

Here α_i is the Polanyi parameter and β indicates the degree of nonuniformity. Then expressions for the rate constants were put in eq.(2).

The two-step mechanism was proposed by Temkin and the kinetic equations for uniform surface and nonuniform surface were deduced a long time ago (see review [7]). As it was shown in ref. [7] eq. (2) is valid only in the case of a uniform surface. In order to obtain this equation in ref. [14] the intermediate steady-state conditions were applied for the case of a uniform surface. The derivation of kinetic equations in the case of a nonuniform surface is much more complicated because in this case it is necessary to use either the distribution function of surface sites (biographical nonuniformity [7]) or to solve together equations for the reaction rate which include values of θ and for the steady-state conditions (induced nonuniformity [7]). In ref. [14], steady-state conditions were used as if reaction occurs on a uniform surface and there is no nonuniformity, but the reaction rate is

expressed as if reaction occurs with nonuniformly reactive adsorbates. It means that validity of *all* conclusions in refs. [14,15] which are based on eq.(1) is suspect. For example, the optimum surface coverage was obtained in ref. [14] in the case when Polanyi parameters for both steps are equal and the optimum value of the surface covering was found equal to the Polanyi parameter. Thereby, in ref. [14] volcano curves were discussed in terms of nonuniformity. In ref. [18] an exact analytical solution for the optimum surface coverage for the two-step mechanism in the case of a uniform surface was obtained and it was shown that the optimum value is equal to the Polanyi parameter (if they are the same for both steps). It means that description of volcano-shaped curves (or Sabatier's principle) is even possible when the surface is assumed to be uniform.

5. Surface electronic gas model

As it was shown in refs. [9,12,13] a simple calculation in the spirit of Sommerfeld's theory of metals, but for the two-dimensional case leads to the equation

$$\varepsilon = \varepsilon^0 - \eta^2 \frac{h^2 L}{4\pi m^*}\theta, \tag{4}$$

where η is the effective charge acquired by an adsorbed particle, h is the Planck constant, L is the number of adsorption sites on the unit surface, ε is the heat of adsorption, m^* the effective electron mass. In the supposition that the effective charge was constant the equation was obtained for the adsorption isotherm [13], which for the region of medium coverages approximates the logarithmic isotherm.

The surface electronic gas model was also applied to heterogeneous kinetics [19], when the interaction effects of chemisorbed particles were described in terms of the surface electronic gas model and the surface was assumed to be covered with only one type of adsorbed species.

According to refs. [10,20], in the surface electronic gas model the dependence of the configuration enthalpy of the transient state ($\Delta H^{=}$) on the configurational enthalpy of adsorbed species (ΔH) is expressed as

$$\Delta H^{=}/\Delta H = \eta^{=}/\eta = \alpha. \tag{5}$$

Here α corresponds to the Polanyi parameter, η and $\eta^{=}$ are effective charges in adsorbed and transient states.

As it was shown in ref. [7], the kinetics of several heterogeneous catalytic reactions can be described using the two-step model, assuming biographical nonuniformity. It was demonstrated in ref. [21], that the same form of reaction equation can be deduced for the two-step sequence in the case of induced nonuniformity. These results together with the thermodynamical data discussed above justify application of the surface electronic gas to the problems of structure insensitivity.

6. Structure insensitivity in catalytic hydrogenation

In ref. [14] the correlation between the Polanyi parameter and structure sensitivity based on eq.(1) was also proposed. According to ref. [15] when the catalytic rate is largely controlled by the thermodynamics (α is closed to unity) the nonuniformity effect on the rate is small (the reaction is structure insensitive) and conversely when the thermodynamic effect is small (α closer to zero) the rate is more responsive to the nonuniformity (the reaction is structure sensitive). It follows from the correct equations for the rate [7,20] that, if the reaction corresponds to a two-step mechanism, when the Polanyi parameter is either 0 or 1 the description of the reaction rate does not correspond to the case of uniformly reactive adsorbates, which means that it is not possible to explain structural sensitivity only by low values of α and structural insensitivity by values of α close to unity in the case of a two-step mechanism.

As it is well known catalytic hydrogenation of alkenes is an example of a structure insensitive reaction [1–5,8]. If one applies the Horiuti–Polanyi mechanism [22] the nature of insensitivity in this case in terms of induced nonuniformity (particular surface electronic gas model) is not clear, because at any values of α reaction rate depends on values of $h^2\eta^2/4\pi m^*$, which must be different at different values of catalyst particle sizes.

Recently [23] another model was proposed for the description of the liquid-phase hydrogenation of alkenes,

1. $ZA + H_2 = ZAH_2$
2. $ZAH_2 = ZB$
3. $ZB + A = ZA + B$

$$A + H = B, \qquad \text{(II)}$$

where A is the substrate, B the product, AH_2 an intermediate complex, and stage 3 is equilibrium. We note that this mechanism explains the simultaneous zero orders with respect to A and H_2, because it assumes the formation of a complex AH_2 on the surface of the catalyst which slowly isomerizes into B. At high values of hydrogen partial pressures the surface of the catalyst is completely covered with this complex and the reaction rate ceases to depend on either hydrogen pressure or the concentration of A. The nature of the proposed complexes on the surface of the catalyst can be explained using the "aromaticity principle" proposed in ref. [24] which forms the basis of the multiplet theory of Balandin. According to this principle in heterogeneous catalysis reaction occurs predominantly through intermediate compounds or transition states in which the atoms of the reactants and the catalyst form rings having aromatic character. ZAH_2 could be a doublet complex containing two atoms of the catalyst.

In ref. [23] the surface was considered as uniform or quasi-uniform. Now we con-

sider this mechanism using the surface electronic gas model. Let us assume for the simplification in derivation of kinetic equations that each molecule occupy only one elementary space, the effective charges of adsorbed particles are constant and

$$\eta_{\mathrm{A}}^{=(1)} = \eta_{\mathrm{AH}}^{=(1)} = \eta_{\mathrm{AH}}^{=(2)} = \eta_{\mathrm{A}}^{=} = \alpha\eta_{\mathrm{A}} = \alpha\eta_{\mathrm{AH}} = \alpha\eta\,. \tag{6}$$

Using the balance equation

$$\theta_{\mathrm{A}} + \theta_{\mathrm{AH}} + \theta_{\mathrm{B}} = 1\,, \tag{7}$$

we arrive to

$$r_1 = k_1 P\theta_{\mathrm{A}} \exp[(1-\alpha)\eta^2 C/T]\,, \tag{8}$$

$$r_{-1} = k_{-1}\theta_{\mathrm{AH}} \exp[(1-\alpha)\eta^2 C/T]\,, \tag{9}$$

$$r_2 = k_2\theta_{\mathrm{AH}} \exp[(1-\alpha)\eta^2 C/T]\,, \tag{10}$$

$$K_3 = N_{\mathrm{B}}\theta_{\mathrm{A}}/N_{\mathrm{A}}\theta_{\mathrm{B}}\,, \tag{11}$$

where N_{A} and N_{B} are the mole fractions of A and B, k_1 and k_{-1} are the rate constants of elementary reactions of step 1, etc., K_3 is the equilibrium constant of step 3, P is the hydrogen pressure and C a constant. Then the rate of the liquid-phase hydrogenation is expressed as

$$r = \frac{[k_1 k_2 P N_{\mathrm{A}}/(k_{-1}+k_2)]\exp[(1-\alpha)\eta^2 C/T]}{N_{\mathrm{A}} + [k_1 P N_{\mathrm{A}}/(k_{-1}+k_2)] + K_3^{-1} N}\,. \tag{12}$$

With $\alpha = 1$ we arrive to the equation which was deduced in ref. [23] using the assumption of uniform or quasi-uniform surface. With such values of α the reaction is structure insensitive. In terms of the surface electronic gas model it means that effective charges of adsorbed species and activated complexes in transition state are equal.

We must note that even for hydrogenation of olefins this explanation cannot be the only one, depending on the reaction mechanism. For instance the hydrogenation of ethylene over a wide variety of platinum catalysts shows structure insensitive behaviour [5]. However, in this case carbonaceous deposits can be formed on the surface of the catalyst and the hydrogenation process can occur on the top of this carbonaceous layer. Evidently concepts of surface electronic gas cannot be applied for such a reaction.

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