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Non-equilibrium effects in the liquid-phase catalytic hydrogenation

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Abstract

Catalytic hydrogenation in the liquid-phase over supported metal catalysts at high hydrogen pressures can be described by the zero order in respect to all components. The reaction mechanism which involves formation of intermediate complexes including hydrogen and organic compound is discussed. The reaction rate in the region of zero orders is determined by the isomerisation rate of these complexes. Experimental data presented indicate that the pre-exponential factor in Arrhenius equation is essentially less then expected from the absolute rate theory. These observations are explained based on the model of an anharmonic oscillator.

1. Introduction

The kinetics of heterogeneous catalytic reactions are extensively studied. The challenging objective in such studies regarding the mechanism of reactions is obtaining full information on kinetic parameters characterizing elementary steps of a reaction. One of the fundamental questions which have to be answered is what the values of Arrhenius parameters are and if it is possible to predict their values.

One of the most widely spread theories which is often employed is the transition-state theory [1,2]. This theory represents one of the principal bases of chemical kinetics on solid surfaces [3,4]. The pre-exponential factor of the rate constant was estimated for several elementary processes such as adsorption, desorption and chemical reaction [5–7].

This theory is applied only to equilibrium processes, assuming statistical equilibrium between reactants and activated complexes. As it was demonstrated in literature in many cases TST fails to predict the pre-exponential factors of the rate constants of a given process and therefore a concept of transmission coefficients for nonadiabatic processes is employed [8,9]. In instance of heterogeneous catalytic reactions the importance of taking into account transmission coefficients, mainly based on the Landau–Zener model [10–13], was emphasized in several papers [4,14,15], although as it was pointed out in Ref. [4] there is practically no application of derived formula for transmission coefficients to real surface processes.

However, application of this coefficient contradicts with basic principles of TST, namely statistical equilibrium between reactants and activated complexes. Several models which take into account possible non equilibrium effects were advanced in the literature. The rate process can be limited by coupling the reaction system to the bath

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and based on the stochastic modeling [16] an enormous amount of work appears [17]. The non equilibrium models were used also for describing the processes on solid surfaces [18–21].

Closing this section we must note that the information on non equilibrium processes in heterogeneous catalysis is rather scarce and therefore we intend to present some of our data on catalytic hydrogenation related to this subject.

2. Kinetics and mechanism of catalytic hydrogenation

In the recent years we extensively investigated kinetics of the liquid-phase hydrogenation of different organic compounds on noble metals [22–26]. It was demonstrated that at high hydrogen partial pressures the reaction order towards hydrogen and organic compound is equal to zero. The kinetics were described in instance of alkenes with the following kinetic scheme:

$$\begin{array}{l} 1.\ ZA+H_2 \Leftrightarrow ZAH_2 \\ 2.\ ZAH_2 \Rightarrow ZB \\ \underline{3.\ ZB+A \equiv ZA+B} \\ A+H_2 = B \end{array} \qquad (1)$$

where Z is a surface site, A is the substrate, B is the product, AH_2 an intermediate complex, stage 3 is an equilibrium one. 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 is 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 role of hydrogen in catalytic hydrogenation can be viewed in the following way. The Group VIII are known to adsorb considerable quantities of hydrogen rapidly. According to Ref. [22] the state of the adsorbed hydrogen resembles that of hydrogen dissolved in Pd, except that it is present within a few atomic diameters of the surface and not in the whole bulk of the metal. The existence of subsurface sites in chemisorption was proposed in the literature on the basis of velocity distribution of desorbing hydrogen, angle resolving photoelectron spectroscopy and binding states in TPD [27]. The hydrogen does not compete for sites with the molecules adsorbed on the surface. If the adsorbed hydrogen is in equilibrium with the hydrogen dissolved in the liquid phase the reaction rate will not depend on the extent of filling of the sites for hydrogen adsorption. That means that from the viewpoint of transition state theory activated complexes will be in equilibrium with both the adsorbed and the dissolved hydrogen. As it was pointed out in Ref. [22] the reaction rate will be the same whether the activated complexes are formed from the adsorbed hydrogen or from the dissolved hydrogen, therefore it is convenient to express the reaction rate as a function of hydrogen pressure in the gas phase in equilibrium with the liquid phase rather than as a function of hydrogen concentration in the liquid phase. Following Ref. [22] in the derivation of kinetic equations it is assumed that the surface of the catalyst is uniform or quasi-uniform and organic compounds form an ideal liquid mixture, hence their activities are equal to their mole fractions. The mole fraction of hydrogen in the liquid phase can be neglected, because its solubility is low.

The reaction rate r obeys the following equation:

$$r=kP_{H_2}N/(N+k'P_{H_2}+k''(1-N)) \qquad (2)$$

where N is the mole fraction of A in the mixture with B, k, k' and k'' are constants

$$k=k_1k_2/(k_{-1}+k_2);$$

$$k'=k_1/(k_{-1}+k_2); \quad k''=K_3^{-1} \qquad (3)$$

Here k_1 is the rate constant for stage 1 in the forward direction, etc.

In the instance of aromatic compounds the formation of adsorbed cyclohexadiene or its derivatives is forbidden by thermodynamic reasons

[22]. The calculations, performed in [22] showed, that the equilibrium constant for gas-phase benzene hydrogenation into cyclohexadiene-1,3 is 10^{-10} order of magnitude at the range 323–423 K. As the vapor pressures of hydrocarbons, e.g. benzene and cyclohexadiene, differ only slightly the reaction in consideration can hardly occur. Although there are no values in the literature concerning the heat of adsorption of cyclohexadiene, there is no reason to suppose that it will be considerably greater than one for benzene by about 70 kJ/mole. Another explanation could be that the rate of cyclohexadiene hydrogenation must exceed the rate of stage 1 in mechanism 1 in reverse direction by a factor of about 10^{10} which is impossible.

Therefore an alternative mechanism was advanced in [22] which does not involve the intermediate formation of cyclohexadiene or derivative, allows the intermediate formation of cyclohexene [29] and accounts for reaction kinetics. It was proposed, that a second intermediate complex $A(H_2)_2$ is formed from AH_2. Only isomerisation of $A(H_2)_2$ in the adsorbed state to form cyclohexene occurs. The kinetic equations corresponding to that mechanism were tested and showed good accuracy in description of experimental data in instance of the liquid-phase benzene hydrogenation over Ni/C [23,24], Ni/Cr_2O_3 [28] and over carbon supported Pt, Pd, Ir, Ru, Rh [29]; phenol hydrogenation over Pt [25], Ni [30], Pd [31], 4-*tert.*-butylphenol hydrogenation over Rh [26] and thymol hydrogenation over Rh, Pt, Ir [32].

From the above presented considerations it follows, that the reaction rate of catalytic hydrogenation in the case of zero orders towards organic compounds and hydrogen is determined by the isomerisation of intermediate complexes which have an aromatic character.

3. Aromaticity principle in catalysis

The nature of intermediate complexes on the surface of the catalyst can be considered using the 'aromaticity principle' which was proposed by M.I. Temkin for explanation of the Balandin's multiplet theory of heterogeneous catalysis [33]. According to this principle, in heterogeneous catalysis, the reaction occurs predominantly through intermediate compounds or transition states in which the atoms of the reactants and the catalyst form rings having an aromatic character. For example complex ZAH_2 could be a doublet complex containing two atoms of catalyst and it resembles naphthalene derivative. Such complex is formed without loosing the aromatic benzene ring with some additional resonance energy. The idea of aromaticity of transition state was advanced by Evans [34] in the instance of homogeneous non catalytic reactions as long as in 1939 and further developed and applied for Diels–Alder reactions, i.e. the addition of 1,3-butadiene to maleic anhydride. The unusual ease of this reaction was explained by the formation of transition state, having aromatic character. In contrast to Evans it was proposed by Temkin, that not only transition state but intermediate complex in heterogeneous catalytic reaction could have an aromatic character. It was pointed out in Ref. [33], that for the atomic orbitals to overlap special geometric requirements must be fulfilled and the atoms must be located at least approximately in a single plane, thus explaining Balandin's principle of geometric correspondence.

4. Experimental data

Before presenting experimental data we would like to describe briefly the experimental setup which was used during the course of hydrogenation studies.

The kinetic experiments were performed in a shacked reactor with an external heating–cooling system. The volume of the reactor was 75 or 150 ml. The frequency of vibration of the reactor was 150 min^{-1} and the amplitude was 15 cm. The pressure in the reactor was measured with a standard manometer and was constant during the experiment. The reactor temperature was kept

Table 1
Kinetic parameters for the liquid-phase hydrogenation

Substrate	Catalyst	r (mole/g h)	k (s^{-1})	E_{act} (kJ/mole)	Ref.
Benzene	Pt	$5.3 \cdot 10^3$	$2.9 \cdot 10^4$	19530	[36]
Benzene	Pd	$1.8 \cdot 10^5$	$5.9 \cdot 10^5$	41480	[37]
Benzene	Rh	$4.2 \cdot 10^6$	$1.4 \cdot 10^7$	31983	[38]
Benzene	Os	$1.5 \cdot 10^9$	$1.2 \cdot 10^{10}$	66045	[39,40]
Benzene	Ni	$4.0 \cdot 10^7$	$6.7 \cdot 10^7$	61466	[23]
Cyclohexene	Ni	$5.5 \cdot 10^6$	$9.3 \cdot 10^6$	46000	[41]
Cyclohexene	Pd	$1.2 \cdot 10^7$	$5.0 \cdot 10^8$	40800	[42]
Cyclohexene	Pt	$4.0 \cdot 10^8$	$1.1 \cdot 10^{10}$	46900	[42]
Benzoic acid	Pd	$6.8 \cdot 10^5$	$2.8 \cdot 10^6$	51300	[43]
Phenol	Pd	$1.0 \cdot 10^5$	$5.5 \cdot 10^5$	41300	[44]
Phenol	Ni	$3.5 \cdot 10^4$	$5.9 \cdot 10^4$	53600	[30]
4-*tert.*-Butylphenol	Rh	$1.4 \cdot 10^8$	$4.1 \cdot 10^8$	48800	[26]

within a range of 1 K of the fixed values. The hydrogenation reactions were carried out between 300 and 473 K and at hydrogen pressures between 0.1 and 6 MPa depending on the substrate. Before an experiment, the reactor containing the substrate and catalyst was flushed with H_2 at room temperature (for 1 h). During the course of the reaction samples of the solution were taken and analyzed by FID gas chromatography. A fresh portion of catalyst was taken for each experiment.

The absence of diffusion limitations was verified using the published procedure [35]. The proportionality of the efficiency of the reactor to the amount of catalyst, the calculation of the rate of diffusion of dissolved hydrogen to the outside surface of the catalyst particles, and the efficiency factor show that the reaction took place in the kinetic region.

At high hydrogen partial pressures the reaction orders towards hydrogen and substrate are equal to zero. The reaction rate (r) is thus determined by the isomerisation reaction in the adsorbed state and is equal to the constant of that reaction. The values of pre-exponential factors for the constants in the region of zero orders with respect to organic compounds and hydrogen were calculated taking into account the surface area of the catalysts; they are given in Table 1.

The values reported in the Table 1 are far from the expected values of 10^{12} s^{-1} for the pre-exponential factor of the isomerisation reaction in the adsorbed state [4–7].

5. Model of anharmonic oscillator

Recently Bond [45] discussed the source of the activation energy in catalyzed reactions in connection with the compensation effect. According to his treatment this source is thought to be of the lattice vibrational modes (phonons) which form a 'heat bath' from which adsorbed entities are activated to the transition state.

Quantitative description of the compensation effect due to vibrational relaxation processes in some special cases was given by B. McCoy [46–48] and within the framework of this approach we will try to explain the non equilibrium effects in the liquid-phase hydrogenation.

According to McCoy [46,48] in heterogeneous catalytic reactions which involves breaking of chemical bonds, catalyzed dissociation steps could be treated taking into account the anharmonic nature of the oscillating bound species and interaction with the catalyst.

Chemical species in the molecule can oscillate about the bond because of collisions with the thermal bath. For heavy species the vibrational energy levels can form a near continuum of vibrational energy states. McCoy [46,48] solved the differential form of the master equation for the anharmonic oscillator and deduced the following expression for the rate constant k

$$k = (R_p s_p^p / (1 + \alpha s_n)) \times (\beta h \omega_o / 2\pi)^2 \exp(-\beta E_{act}) \qquad (4)$$

where ω_o is the energy level spacing for an harmonic oscillator, α is the anharmonicity parameter, $R_p s_p^p$ is the transition probability describing the effect of the bath, h is the Planck constant, β is the Boltzmann constant, s is a continues variable and s_n is the energy level at which the molecule dissociates.

For the case $p = 2$ and $\alpha s_n \gg 1$, taking into account that $R(s) = 10^{13}$ s^{-1} [49] the pre-exponential factor for the Arrhenius equation was found to be [47] 10^{13} s^{-1} which corresponds to the transition state theory.

Applying the model to the catalytic hydrogenation we assume that in the proposed complexes the reaction rate of isomerisation is determined by the dissociation of the hydrogen–hydrogen bond. As the activation energy for the studied hydrogenation reactions is 40–50 kJ/mole, it follows from Eq. (4) that the main non equilibrium effect for the presented data, e.g. for the fact that observed values of the pre-exponential factor are essentially less then 10^{12} s^{-1}, is due to the transition probability $R(s)$. We propose therefore that in the instance of organic compounds hydrogenation when the intermediate complexes having aromatic character are involved, the transition probability is lowered. Due to the additional overlap the stability of complexes could be extremely high, thus lowering the pre-exponential factor in the Arrhenius equation.

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