On the rate of heterogeneous catalytic reactions with ionic intermediates

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A facile way to compute the rate law of a catalytic reaction with ionic intermediates is proposed, based on the theory of complex reactions. When the ionic nature of intermediates is taken into account it is necessary to add balance equations which correspond to the electroneutrality of the catalyst. Several mechanisms of the olefin hydrogenation were considered as examples.

Keywords: Rate laws; heterogeneous catalysis; ionic intermediates; theory of complex reactions

1. Introduction

Catalytic reaction generally consists of several elementary reactions. Therefore, for the description of the reaction mechanism, adsorbed intermediate species are always considered. Such species can have either nonionic or ionic character. Some mechanistic aspects of reactions with ionic intermediates on nonmetals were discussed for different reactions [1–4]. In the case of catalytic hydrogenation on oxides or sulfides, for example, it was proposed that reaction proceeds through cationic intermediates [1]. Ionic species can be involved also in catalytic reactions on metals. Carbocations were proposed as intermediates in neopentane conversion over electron-deficient palladium [5].

Quantification of such mechanistic ideas is essential for description of the surface chemistry. One of the tools for the investigation of a reaction mechanism is kinetics [6–8]. Such kinetical studies are not only necessary from a fundamental point of view, but can also immediately be applied in process optimization and design. Rather often kinetics of heterogeneous catalytic reactions is described using either Langmuir–Hinshelwood or Rideal–Eley concepts [7]. According to the first concept the most likely mechanism involves surface reaction between adsorbed species. In contrast to this, the Rideal–Eley mechanism assumes that the surface reaction occurs as a result of the collision between a fluid-phase molecule

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and an adsorbed one. One of the approaches, which is widely used, is the Hougen–Watson formalism [9]. In this case one of the elementary reactions is considered to control the rate. Frequently, with such simplifications, rate equations cannot reflect essential features of the reaction mechanism.

The recent development of computer-aided analysis of experimental data for heterogeneous catalytic reactions [10] provides possibilities for using accurate kinetical models without Hougen–Watson simplification. Such design of the mathematical models is based on the theory of complex reactions [11,12]. In this procedure the possible ionic nature of adsorbed species is not taken into account; this requires the development of derivation of kinetic expressions for such cases. Recently [13] an attempt was made to describe the reaction of catalytic reactions involving ionic intermediates using Langmuir–Hinshelwood Hougen–Watson approach.

The aim of the present paper is to generalize the procedure of kinetic computations using the theory of complex reactions when ionic surface species exist. Such analysis is valid either for Langmuir–Hinshelwood or Rideal–Eley concepts without Hougen–Watson simplifications.

2. Results and discussion

2.1. GENERAL CONSIDERATIONS

Firstly we will recall some definitions of the theory of complex reactions. Elementary reactions of a complex reaction are grouped into steps. Chemical equations of the steps contain reaction participants and intermediates (i.e. surface species). Overall reaction equations can be obtained by addition of chemical equations of steps multiplied by stoichiometric numbers (positive, zero or negative). Such numbers must be chosen in a way that the overall equations contain no intermediates. A set of stoichiometric numbers of steps producing overall equation was called a reaction route [12]. Relations between surface coverages of species are called balance equations. For example the total surface coverage of sites can be equal to unity. If there are two types of sites there will be two balance equations. The following equation for the determination of the number of basic routes P was proposed in ref. [12]:

$$P = S + W - J, \tag{1}$$

where S is the number of steps, W is the number of balance equations, and J is the number of intermediates.

2.2. FIRST EXAMPLE

Let us now consider the model of hydrogenation of olefin R on oxides and sulfides with heterolytic dissociation of hydrogen, basing on mechanistic considerations, proposed in ref. [1],

$$\begin{array}{ll} 1.\ H_2+Z+Z' \rightarrow ZH^- + Z'H^+ & 1 \\ 2.\ ZH^- + R \rightarrow ZRH^- & 1 \\ 3.\ ZRH^- + Z'H^+ \rightarrow Z+Z'+RH_2 & 1 \\ \hline R+H_2 = RH_2\,. & \end{array} \tag{2}$$

Symbols Z and Z′ correspond to surface coverage of different sites. These sites can be surface cation and anion respectively. On the right side of the reaction steps stoichiometric numbers are written. For convenience, elementary reactions are considered to be irreversible.

As it is seen from this scheme there is only one route, five intermediates (Z, Z′, ZH^-, $Z'H^+$ and ZRH^-) and three steps. According to eq. (1) there must be three balance equations. If there are two types of sites we have two balance equations,

$$[Z]+[ZH^-]+[ZRH^-]=1\,, \tag{3}$$

$$[Z']+[Z'H^+]=1\,. \tag{4}$$

Besides these two balance equations, which corresponds to the fact that the total coverages are equal to unity, one more balance equation exists. This latter balance equation must correspond to the fact that catalyst is electroneutral. In the case of scheme (2) this means that

$$[ZH^-]+[ZRH^-]=[Z'H^+]\,. \tag{5}$$

From eqs. (3)–(5) we can easily obtain that

$$[Z]=[Z']\,. \tag{6}$$

In steady-state conditions the rate of all steps divided by their stoichiometric numbers is equal to the rate of the overall reaction [11,12]. Therefore the following equations can be written:

$$k_1 P_H [Z][Z'] = k_2 [ZH^-] P_R\,, \tag{7}$$

$$k_1 P_H [Z][Z'] = k_3 [ZRH^-][Z'H^+]\,, \tag{8}$$

where P_H and P_R are partial pressures of hydrogen and olefin respectively.

From eqs. (3)–(8) we can obtain

$$[Z] \pm \frac{k_1 P_H}{k_2 P_R}[Z]^2 \pm \frac{k_1 P_H}{k_3 (1-[Z])}[Z]^2 = 1\,. \tag{9}$$

Three real values of surface coverages can be obtained as a solution of this equation, depending on values of constants and pressures. This unexpected conclusion regarding multiplicity cannot be obtained from classical treatment. Such multiple steady states in reaction rate were observed in the case of CO oxidation at intermediate CO pressures over supported noble metals [14], where this multiplicity is obviously of another origin.

2.3. SECOND EXAMPLE

Another model for olefin hydrogenation can be considered basing on the mechanism proposed in refs. [2,3] for diene, aldehyde and ketone hydrogenation over copper chromite catalysts. It can be written in a following way:

$$\begin{array}{ll} 1.\ \mathrm{H_2 + ZZ' \rightarrow ZH^- Z'H^+} & 1 \\ 2.\ \mathrm{ZH^- Z'H^+ + R \rightarrow ZZ'H^+ : RH^-} & 1 \\ 3.\ \mathrm{ZZ'H^+ : RH^- \rightarrow ZZ' + RH_2} & 1 \\ \hline \mathrm{R + H_2 = RH_2}\,. & \end{array} \tag{10}$$

In such a model, negative species $\mathrm{RH^-}$ were considered to be adsorbed on a site with a positive charge. From the kinetic point of view the description in this case is the same as if we consider a reaction with nonionic intermediates. Hence we have only one route, three steps and three intermediates, which can be considered as neutral ($\mathrm{ZZ'}$, $\mathrm{ZH^- Z'H^+}$, $\mathrm{ZZ'H^+ : RH^-}$) and therefore only one balance equation which corresponds to the total surface coverage equal to unity. In this case a classical version of the theory of complex reactions can be used for the rate law computations. Such a procedure was, for example, recently used for the rate law computation for benzene hydrogenation with cyclohexane and cyclohexene formation [15].

2.4. THIRD EXAMPLE

Kinetics of hydrogenation of olefins on oxides was discussed in ref. [13] where the Langmuir–Hinshelwood–Hougen–Watson formalism was used. The mechanism from ref. [13] is presented below for convenience in a form where all stoichiometric numbers are equal to unity:

$$\begin{array}{ll} 1.\ \mathrm{R + M^+{-}OH^- \rightleftharpoons M^+{-}ORH^-} & 1 \\ 2.\ \mathrm{M^+{-}ORH^- + M^+H^- \rightarrow M^+{-}RH_2 + M^+{-}O^{2-}} & 1 \\ 3.\ \mathrm{M^+{-}RH_2 \rightleftharpoons M^+ + RH_2} & 1 \\ 4.\ \mathrm{H_2 + M^+OH^- \rightleftharpoons H_2O + M^+H^-} & 1 \\ 5.\ \mathrm{H_2O + M^+ + M^+{-}O^{2-} \rightleftharpoons 2M^+{-}OH^-} & 1 \\ \hline \mathrm{R + H_2 = RH_2}\,. & \end{array} \tag{11}$$

Steps 1, 3–5 are equilibrium steps and step 2 is the rate-determining one. The symbol $\mathrm{M^+}$ corresponds to the cation, $\mathrm{M^+{-}O^{2-}}$ is surface oxygen. As it is seen from this scheme there is only one route, six intermediates and five steps. According to eq. (1) there must be two balance equations, one for the total coverage of surface species and another one corresponds to the electroneutrality of the catalyst,

$$M^+ + M^+{-}RH_2 = M^+{-}O^{2-}\,. \tag{12}$$

Now it is possible to obtain the equation for the reaction rate. It can be written in a following way:

$$r = \frac{K_1 k_2 K_4 [R][H_2][H_2O]}{\{[H_2O] + K_1[R][H_2O] + 2(K_5)^{-0.5}((1 + K_3[RH_2])([H_2O]))^{0.5} + K_4[H_2]\}^2}\,. \tag{13}$$

Though eq. (13) was previously obtained in ref. [13], the difference between ref. [13] and the present paper is that our treatment using the theory of complex reactions illustrates how many balance equations are necessary for rate law computation. This point was not clarified in ref. [13] and the balance equations were referred to as approximation.

The theory of complex reactions with additional balance equations gives also the possibility of computing the rate law of catalytic reactions with ionic intermediates when it is important to take into account participation of the bulk of the catalyst [16]. In this case, from the view point of the theory of complex reactions it means that besides the balance equation which corresponds to total electroneutrality of surface species, there will be another one which describes the electroneutrality of the whole catalyst.

3. Conclusion

Computation of reaction rates for reactions involving ionic species can be easily done using the theory of complex reactions [11,12]. The only difference between such computation and the classical one is that in this case it is necessary to add balance equations which correspond to the electroneutrality of the catalyst. This approach is a general one and allows computation of the rate laws without any approximation.

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