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Chemical Kinetics of Catalyzed Reactions: A Review.

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ABSTRACT

Chemical kinetics is a key subdiscipline of physical chemistry that studies the reaction rate in every elemental step and corresponding catalytic mechanism. It mainly concludes molecular reaction dynamics, catalytic dynamics, elemental reaction dynamics, macrodynamics, and microdynamics. Such a research field has wide applications in heterogeneous catalysis. Through the study of chemical kinetics, it can reasonably guide us to know how to control the reaction conditions and improve the main reaction rate, in order to increase the production of chemical products, and also guide us to learn how to suppress or slow down the reaction rate of side reactions to reduce the consumption of raw materials, reduce the burden of separation operations, and eventually improve the product quality. Chemical kinetics can provide general knowledge on how to avoid explosion of dangerous goods, material corrosion, and aging and deterioration of products. It can also carry out optimal design and control for the industrialization of scientific research results and select the most suitable operating conditions for the existing production.

Keywords: chemical kinetics, reaction rate, heterogeneous catalysis, petrochemical industries.

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Introduction

Heterogeneous catalysis is of vital importance to the world's economy, allowing us to convert raw materials into valuable chemicals and fuels in an economical, efficient, and environmentally benign manner. For example, heterogeneous catalysts have numerous industrial applications in the chemical, food, pharmaceutical, automobile and petrochemical industries [1–5], and it has been estimated that 90% of all chemical processes use heterogeneous catalysts [6]. Heterogeneous is also finding new applications in emerging areas such as fuel cells [7–9], green chemistry [10–12], nanotechnology [13], and biorefining/biotechnology [14–18]. Indeed, continued research into heterogeneous catalysis is required to allow us to address increasingly complex environmental and energy issues facing our industrialiazed society.

Discussing the principles of heterogeneous catalysis is difficult, because catalysts are used for a wide range of applications, involving a rich range of surface chemistries. Moreover, the field of heterogeneous catalysis is highly interdisciplinary in nature, requiring the cooperation between chemists and physicists, between surface scientists and reaction engineers, between theorists and experimentalists, between spectroscopists and kineticists, and between materials scientists involved with catalyst synthesis and characterization. Furthermore, industrial catalysts are complex materials, with highly optimized chemical compositions, structures, morphologies, and pellet shapes; moreover, the physical and chemical characteristics of these materials may depend on hidden or unknown variables.

Accordingly, principles of heterogeneous catalysis are typically formulated from studies of model catalysts in ideal reactors with simplified reactants under mild pressure conditions (e.g., 1 bar), rather than from catalytic performance data obtained with commercial catalysts in complex reactors using mixed feed streams under industrial reaction conditions. The principles derived from these more simplified studies advance the science of heterogeneous catalysis, and they guide the researcher, inventor, and innovator of new catalysts and catalytic processes.

The definition of a catalyst has been discussed many times [19]. For example, a catalyst is a material that [converts reactants into products, through a series of elementary steps, in which the catalyst participates while being regenerated to its original form at the end of each cycle during its lifetime. A catalyst changes the kinetics of the reaction, but does not change the thermodynamics. Another definition is that a catalyst is a substance that transforms reactants into products, through an uninterrupted and repeated cycle of elementary steps in which the catalyst participates while being regenerated to its original form at the end of each cycle during its lifetime (20).

The main advantage of using a heterogeneous catalyst is that, being a solid material, it is easy to separate from the gas and/or liquid reactants and products of the overall catalytic reaction. The heart of a heterogeneous catalyst involves the active sites (or active centers) at the surface of the solid. The catalyst is typically a high-surface area material (e.g., 10–1000 m2 g−1), and it is usually desirable to maximize the number of active sites per reactor volume.

Identifying the reaction intermediates – and hence the mechanism – for a heterogeneous catalytic reaction is often difficult, because many of these intermediates are difficult to detect using conventional methods (e.g., gas chromatography or mass spectrometry) because they do not desorb at significant rates from the surface of the catalyst (especially for gas-phase reactions).

Heterogeneous catalysts typically contain different types of surface sites, because crystalline solids exhibit crystalline anisotropy. Equilibrated single crystals expose different faces with different atomic structures so as to minimize total surface energy. It would be surprising, in fact, if different crystallographic planes exposing sites with different coordination environments possessed identical properties for chemisorption and catalytic reactions. Moreover, most catalytic solids are polycrystalline. Furthermore, in order to achieve high surface areas, most catalysts contain particles with sizes in the nanometer length scale. The surfaces of these nanoscopic particles contain sites associated with terraces, edges, kinks, and vacancies [21].

Steps in a Heterogeneous Catalytic Reaction

During an overall catalytic reaction, the reactants and products undergo a series of steps over the catalyst, including:

- Diffusion of the reactants through a boundary layer surrounding the catalyst particle.
- Intraparticle diffusion of the reactants into the catalyst pores to the active sites.
- Adsorption of the reactants onto active sites.
- Surface reactions involving formation or conversion of various adsorbed intermediates, possibly including surface diffusion steps.
- Desorption of products from catalyst sites.
- Intraparticle diffusion of the products through the catalyst pores.
- Diffusion of the products across the boundary layer surrounding the catalyst particle.

Accordingly, different regimes of catalytic rate control can exist, including: (i) film diffusion control (Steps 1 and 7); (ii) pore diffusion control (Steps 2 and 6); and (iii) intrinsic reaction kinetics control (Steps 3 to 5) of catalyst performance. In addition to mass transfer effects, heat transfer effects can also occur in heterogeneous catalysis for highly exothermic or endothermic reactions (especially in combustion or steam reforming).

Figure 1 shows a general effect of temperature on the reaction rate for a heterogeneous catalyst. At low temperatures, diffusion through the film and pores is fast compared to rates of surface reactions, and the overall reaction rate is controlled by the intrinsic reaction kinetics.

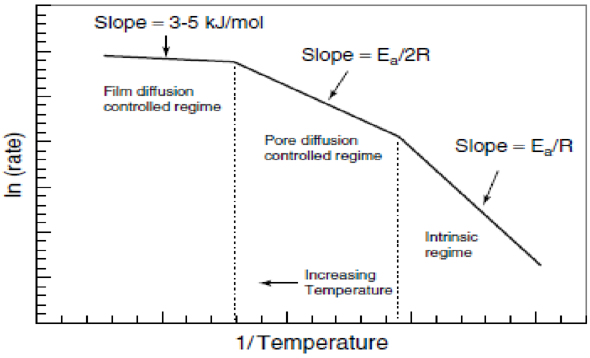

Figure 1: General effects of temperature on catalyst activity. The intrinsic activation energy is equal to (Ea), and R is the gas constant .

As the temperature is increased, the rates of surface reactions typically increase more rapidly than the rates of diffusion, and the overall rate of the catalytic process becomes controlled by intraparticle diffusion.

The apparent activation energy in this regime is equal to the intrinsic activation energy divided by two. As the temperature is increased further, mass transfer through the external boundary layer becomes the controlling step. The onset of diffusion limited regimes can be altered by changing the reactor design, the catalyst pore structure, the catalyst particle size, and the distribution of the active sites in the catalyst particles. Values of various dimensionless groups can be calculated to estimate the extents to which transport phenomena may control catalytic performance for specific operating conditions [23–31]; however, these calculations are most reliable for cases where the intrinsic reaction kinetics are known.

Desired Characteristics of a Catalyst

The following list provides several of the key attributes of a good catalyst:

- The catalyst should exhibit good selectivity for production of the desired products andminimal production of undesirable byproducts.

- The catalyst should achieve adequate rates of reaction at the desired reaction conditions of the process (remembering that achieving good selectivity is usually more important than achieving high catalytic activity).
- The catalyst should show stable performance at reaction conditions for long periods of time, or it should be possible to regenerate good catalyst performance by appropriate treatment of the deactivated catalyst after short periods.
- The catalyst should have good accessibility of reactants and products to the active sites such that high rates can be achieved per reactor volume.

The first three key attributes of a good catalyst are influenced primarily by the interactions of the catalyst surface with the reactants, products, and intermediates of the catalytic process. In addition, other species may form on the catalyst surface (e.g., hydrogen-deficient carbonaceous deposits denoted as coke) that are not directly part of the reaction scheme (or mechanism) for the overall catalytic process.

Concept and Theory of Active Sites

The concept of active sites in heterogeneous catalysis was firstly introduced by Tylor in 1925 [32]. He suggested that only a small fraction of catalyst surface (active sites or centers), which might be composed of an atom or an ensemble of atoms situated at surface defects such as corners, edges, and other crystalline discontinuities, is catalytically active. The idea that the number of active sites is significantly smaller than the total available surface sites was supported by the fact that the amount of poisoning species being required to effectively deactivate a catalyst was often much less than a monolayer coverage of the catalyst surface. This led to the definition of Taylor Ratio (TR) which describes the fraction of active sites out of the total number of catalyst surface sites [33]. In the same period of time, Balandin [34,35] proposed a multiplet theory, suggesting that reacting species could be simultaneously adsorbed to a group of active atoms of catalyst to form a multiplet complex. He also introduced the correspondence between the geometry of active center and the energies of forming and breaking chemical bonds. Proceeding with Taylor's principle of the existence of active sites on catalyst surfaces, Boudart et al. classified reactions in terms of whether they are catalyst surface sensitive or not [36]. The reaction rate of a surface-insensitive process would not change with the exposed planes of a single crystal or the size of particles, whereas that of a surface-sensitive reaction would change significantly. Ethylene hydrogenation catalyzed by platinum is considered as one good example of a surface-insensitive reaction. There have been previous studies over a wide range of dispersions of Pt nanoparticles, as well as single crystals and poly-crystals showing little effects on the reaction rate [33, 37, 38], suggesting all surface Pt atoms are active sites and behave similarly, regardless of their crystallographic planes and locations. On the other side, many other hydrocarbon conversion reactions have also been reported to be surface sensitive [39–41]. Figure 2 shows the structure sensitivity in alkane isomerization reactions catalyzed over platinum single-crystal surfaces [41], which correlates the activity and crystal planes as well as surface atomic ensembles. The results suggest that square surface atom ensembles rather than hexagonal ones favor alkane aromatization and isomerization reactions. One most prominent example of surface-sensitive reaction is ammonia synthesis using iron catalyst.

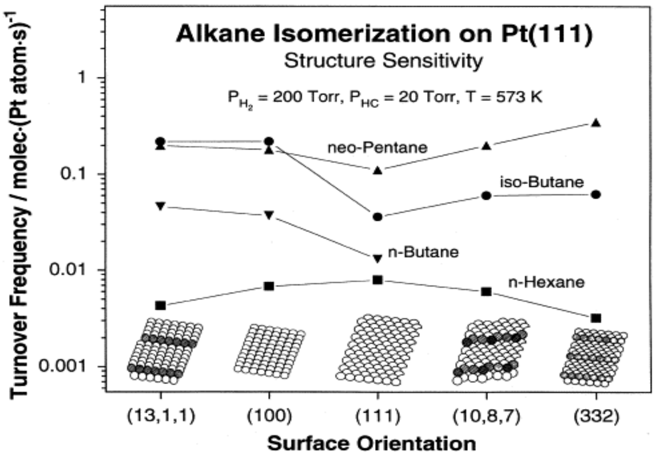

Figure 2: Structure sensitivity in alkane isomerization reaction catalyzed over platinum single crystal surfaces.

Chemical kinetics of catalyzed reactions

Rate expression are indispensable in the application of catalyzed reactions , in the design of chemical processes . in particular reactor design , and in process start –up and control . Insight into the dependence of the reaction rate on catalyst variables ,temperature , and concentration s of product s , and other relevant species is required to predict the size of a catalytic reactor and the optimum operating conditions .

Catalytic reaction pathways consist of reaction sequences formed by a series of Elementary reaction steps . hence ,rate expression are in general a function of many parameters, as depicted in Equ. (1) .

$$r = f\,(\text{catalyst},\ T,\ p_i \text{ or } c_i \ldots, k_i \ldots, K_i \ldots, K_{\text{eq}}) \qquad \ldots\ldots\ldots(1)$$

In heterogeneously catalyzed reactions reactant molecules adsorb on the catalyst surface (characterized by equilibrium constants ki) undergo modification s on the surface to form adsorbed products with rate constants k_i , and these products finally desorb .

The surface composition and structure of the catalyst determine its overall activity and selectivity. Therefore, it is important to relate constants, such as k_i and k_i to the chemical reactivity to the catalyst surface .

Many different modes of adsorption and arrangement of molecule fragments are possible on catalyst surfaces, so many reactions can occur in parallel. Therefore, catalysts may exhibit satisfactory activity but at the same time have a low selectivity. It is common procedure in process development to carry out an optimization program aimed at increasing the selectivity of the catalyst system selected . selectivity can often be increased by the use of promotors or catalyst modifiers to create particular surface sites that enhance the desired reaction but suppress undesired reaction paths.

In homogeneous reaction catalysis ligands play similar role as surface sites with respect to selectivity. In a solution many different catalytic complexes may be present with different catalytic activities. Types and concentrations of ligands determine the structure of the catalyst complexes to a large degree. Thus, catalytic activity and selectivity can be tuned by selecting the right ligands and reaction conditions. Similarly, in biocatalysis enzymes play the role of active sites, having a very high (shape) selectivity for specific reactions.

Beside activity and selectivity, stability is crucial in catalysis applications. Catalyst deactivation can have a kinetics origin. For instance, deactivation might occur by a serial reaction mechanism in which an intermediate can undergo a reaction to form a substance that is a poison for the active catalyst sites. frequently encountered examples are oligomerization and coke formation.

Adsorption on a solid catalyst surface, complex formation in homogeneous catalysis with metallo-organic complexes and in biocatalysis with enzymes share the same principle, i.e. the total number of sites is constant. Therefore, the rate expressions for reactions on heterogeneous, homogeneous and biocatalysts have a similar form. The constant number of active sites results in rate expression that differ from homogeneous gas phase kinetics. Partial pressures are usually used in rate expressions for gas phase reactions, while concentrations are used when the reactions take place in liquid phase. It appears that definitions and nomenclature of particular kinetics constants in the different sub-communities differ sometimes. In the following sections the expressions used by the different subdisciplines will be compared and their conceptual basis outlined.

In the approach to the derivation of rate expressions two principles are important:

- Catalyst do not affect the overall equilibrium of a reaction, but only the reaction rate of the reacting molecules.
- The total number of catalytically active sites is assumed to be a constant. In heterogeneous catalysis this site density is expressed as the number of sites per unit mass of catalyst or per unit surface area , in homogeneous catalysis it is expressed as the concentration of catalytically active

complex molecules, and in biocatalysis as the enzyme concentration. In fact, the above assumption is not always justified. there are examples where the number of active sites is a function of process variables such as temperature and concentration.

Rate Expression (single –site model)

Consider the reversible reaction A↔B (e.g. isomerization), which proceed s according to the three elemental steps represented in fig. 3.

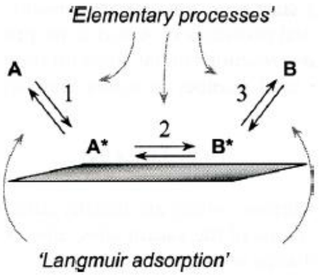

Figure 3: Schematic representation of the reaction A↔B

1. $A + * \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^*$
2. $A^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B^*$
3. $B^* \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} B + *$

This kinetic model can be interpreted as follows:

- Molecule A adsorbs on an active site* at the catalyst surface with formation of an adsorb complex A*.
- The adsorb complex reacts on the active site by rearrangement to an adsorbed complex B*.
- Finally, product B desorbs from the active site, liberating the site for a new catalytic cycle.
- Since these steps are considered to be elementary processes, their rates can be directly derived from their reaction rate expressions.

$$r_1 = r_{+1} - r_{-1} = k_1\, p_A\, N_T\, \theta_* - k_{-1}\, N_T\, \theta_A \qquad \text{……………………(2)}$$

$$r_2 = r_{+2} - r_{-2} = k_2\, N_T\, \theta_A - k_{-2}\, N_T\, \theta_B \qquad \text{………………..(3)}$$

$$r_3 = r_{+3} - r_{-3} = k_3\, N_T\, \theta_B - k_{-3}\, p_B\, N_T\, \theta_* \qquad \text{…………………………..(4)}$$

Note that under steady –state conditions the rate of each reaction step equals the overall net rate, r, θ, θ_A, and θ_B represent the fraction of the total number of sites that are vacant, or occupied by A and B, respectively. N_T represent the total concentration of active sites with possible dimension mol. (kg cat) $^{-1}$. For this gas –phase reaction, partial pressures of A and B are preferred in the rate equation, but for liquid –phase reactions molar concentration should be used. conservation of the total number of active sites leads to the site balance expression:

$$1 = \theta_* + \theta_A + \theta_B \qquad \text{………………..(5)}$$

Under steady –state conditions , which are usually satisfied in continuous –flow processes , the concentrations of the vacant sites ,sites occupied by A , and sites occupied by B, do not change with time

$$\frac{d\theta_A}{dt} = 0 = k_1\, p_A\, \theta_* - k_{-1}\, \theta_A - k_2\, \theta_A + k_{-2}\, \theta_B$$ …………………..(6)

$$\frac{d\theta_B}{dt} = 0 = k_{-3}\, p_B\, \theta_* - k_3\, \theta_B - k_{-2}\, \theta_B + k_2\, \theta_A$$ …………………..(7)

This is equivalent to the fact that under these conditions the net rates of the different steps are the same

$$r = r_1 = r_2 = r_3$$ ………………..(8)

From Eqns. (5-7) , the unknowns θ_*,θ_A ,and θ_B can be expressed as functions of the rate constants and partial pressures and then substituted in Eqn. (8) . finally ,Eqn. (9) follows for the reaction rate expression

$$r = \frac{N_T\, k_1\, k_2\, k_3\, (p_A - p_B / K_{eq})}{(k_1k_3 + k_1k_{-2} + k_1k_2)p_A + (k_{-1}k_{-3} + k_2k_{-3} + k_{-2}k_{-3})p_B + (k_{-1}k_{-2} + k_{-1}k_3 + k_2k_3)}$$ …….(9)

With keq = $k_1k_2k_3$(ki=k_i/ k_{-i}) being the overall equilibrium constant for the reaction .
Rate expression (9) has been derived for a relatively simple kinetic model by application of the site balance and the steady –state hypothesis. More complex models with result in more complex expression s (42,43) for general derivation , which are hard to handle . Fortunately, some simplification s can usually be applied. The rate expression then follows by computing the net rates of intermediate formation r_{ij} which are the sum of the intermediate formation (forward)and intermediate removal (backward) reaction steps:

$$r_i = r_{+i} - r_{-i}$$ ………………(10)

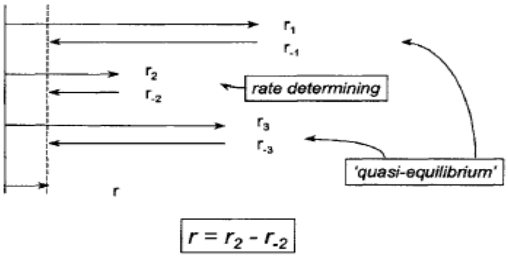

Figure 4 : Visualization of the quasi-equilibrium and rate –determining steps .The length s of the arrow s are proportional to the rates of the relevant steps .

Rate –Determining Step – Quasi- Equilibrium

The a forementioned reaction A↔B proceeds through three elementary processes in series . Consequently, the net rates of the individual steps are equal to the overall rate (8) . It can be imagined that the forward and backward rates of two of these steps are large compared with the third one. They might be so large that these steps can be in quasi- equilibrium. The third, remaining step is then called the rate –determining step (r.d.s.). Figure (4) depicts the situation in which the surface reaction is rate determining, while the adsorption and desorption steps are in quasi-equilibrium.

The rate expression is now obtained as follows . Starting with the rate determining step:

$$r = r_{+2} - r_{-2} = k_2\, N_T\, \theta_A - k_{-2}\, N_T\, \theta_B$$ **………………(11)**

The quasi –equilibrium is then used for the other reaction steps, since

$$\frac{r_1}{r_{+1}} = \frac{r_{+1} - r_{-1}}{r_{+1}} << 1 \qquad \text{……………………………….(12)}$$

$$\frac{r_3}{r_{+3}} = \frac{r_{+3} - r_{-3}}{r_{+3}} << 1 \qquad \text{…………………………….(13)}$$

Substitution of (2) in (12) gives

$$\theta_A = \frac{k_1}{k_{-1}} p_A \, \theta_* = K_1 \, p_A \, \theta_* \qquad \text{…………………(14)}$$

and similarly,

$$\theta_B = \frac{k_{-3}}{k_{+3}} p_B \theta_* = \frac{1}{K_3} p_B \, \theta_* \qquad \text{…………………(15)}$$

This enable the elimination of the unknown quantities θ_A and θ_B from (11) . The remaining θ_* can be eliminated by use of the site balance (5) .

$$\theta_* = \frac{1}{1 + K_1 \, p_A + p_B / K_3} \qquad \text{…………………(16)}$$

The resulting rate expression for the case that the surface reaction is rate determining is given by Eqn. (17) .

$$r = \frac{N_T \, k_2 \, K_1 \, [p_A - p_B / K_{eq}]}{1 + K_1 \, p_A + p_B / K_3} \qquad \text{……………(17)}$$

Similar equations can be derived in case adsorption is the rate –determining step:

$$r = \frac{N_T \, k_1 \, [p_A - p_B / K_{eq}]}{1 + (1 + 1/K_2) \, p_B / K_3} \qquad \text{………………..(18)}$$

Or when desorption is rate determining :

$$r = \frac{N_T \, k_3 \, K_1 \, K_2 \, [p_A - p_B / K_{eq}]}{1 + (1 + K_2) \, K_1 \, p_A} \qquad \text{…………(19)}$$

If, beside reactant A and product B, other species also adsorb on the active sites, they make these sites unavailable for reaction, and hence lower the reaction rate. The effect of such inhibitors (I) should be included in the rate expression and can be summarised for the considered reaction (and surface reaction rate determining) in Eqn. (20).

$$r = \frac{k[p_A - p_B / K_{eq}]}{1 + K_A \, p_A + K_B \, p_B + \sum K_I \, p_I} \qquad \text{……………(20)}$$

Here k_A, K_B and K_I represent the adsorption equilibrium constants of the components A, B and I, respectively; k represent s the apparent (observed) overall reaction rate constant. It will be clear that $K_A = K_1$ and $K_B = 1/k_3$.

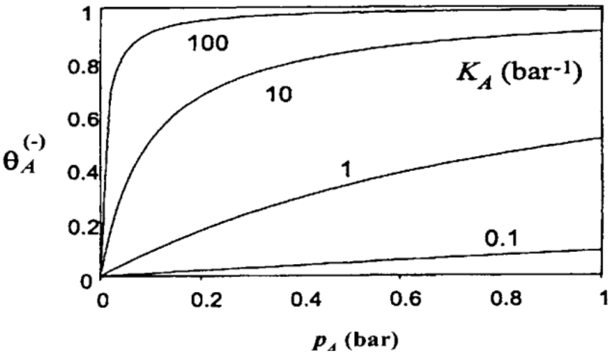

Figure 5: Fractional surface coverage as a function of P_A for several values of K_A .

Adsorption Isotherms

Reaction step (1) in Fig 5 is an adsorption step. Under equilibrium conditions, the net rate is zero and the equilibrium is then described by Eqn. (14). This does not mean per se that K_1 is constant. It may vary with surface occupancy in the case of a non –uniform surface, due to the interaction of adsorbed species with each other. In conventional catalytic kinetics it is generally assumed that one is dealing with a homogeeneous surface. Under the assumptions that

- The surface contains a constant number of identical adsorption sites,
- A site can contain only one molecule; and,
- No interaction takes place between adsorbed molecules, the so –called Langmiur adsorption is operative.

One –component Adsorption

From the foregoing, it can be easily derived that in the case of one – component adsorption, the fractional coverage of the adsorbed species A can be described by Eqn. (21) . Figure (3.3) shows the graphical representation of equation for various values of Ka (≡K_1).

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A} \qquad \text{………………..(21)}$$

Three regions can be distinguished for the Langmuir isotherm

- At low values of $k_A p_A$, a linear relation exists between θ_A and p_A with slope k_A . This is a relation equivalent to Henry's law.
- At high values of $k_A p_A$, θ_A approaches 1 asymptotically, i.e., nearly all sites are occupied . This can be represented by

$$1 - \theta_A = \frac{1}{K_A p_A} \qquad \text{……….(22)}$$

- For values of $k_A p_A$, near 1 , i.e., at moderate coverages , the complete equation (21) must be used . Alternatively, the Freundlich isotherm (23) can be used .
-

$$\theta_A = c\, p_A^{1/n} \qquad (c, n \text{ contants}, n > 1) \qquad \text{……………(23)}$$

With increasing temperature, k_A decreases and a transition from situation 2 to 1 via 3 can be expected. k_A is expressed in units of $(\text{pressure})^{-1}$. If atm $^{-1}$ (1 atm is the standard thermodynamic reference state of gases) is used, k_A can be expressed as :

$$K_A = \exp\left(-\frac{\Delta G_A^\circ}{RT}\right) = \exp\left(\frac{\Delta S_A^\circ}{R} - \frac{\Delta H_A^\circ}{RT}\right) \quad \text{or} \quad \Delta H_A^0 = RT^2 \frac{\partial \ln K_A}{\partial T}$$ …….(24)

In which ΔG°, ΔH°, ΔS° represent the Gibbs free energy, enthalpy and entropy of adsorption, respectively. Both the enthalpy and entropy of adsorption is an exothermic process and the molecule loses at least translational degrees of freedom.

The assumptions for the Langmuir isotherm imply an ideal surface, but few real systems will fulfil this ideal under all conditions. Experimental determination of the heat of adsorption (- ΔH°) as a function of the surface coverage shows that the heat of adsorption usually decreases with increasing coverage. This indicates that catalyst surfaces are not uniform and /or that the adsorbed molecules exhibit a mutual interaction. Adsorption isotherms that take this coverage dependence into account are, amongst others, the Freundlich and the Temkin isotherms. in kinetic modelling practice, these isotherms are hardly used since the derivation of rate expression s becomes a cumbersome job, in particular for multicomponent systems. This situation might rapidly change with the increasing use of powerful computers, but the simple physical picture of the catalyst surface will always remain the advantage of the Langmuir model.

Multicomponent Adsorption

Within the Langmuir approach , the general expression for the fractional coverage by component A in the case of multicomponent adsorption is given by equation (25)

$$\theta_A = \frac{K_A\, p_A}{1 + K_A\, p_A + \sum K_I\, p_I}$$ …………………..(25)

Dissociative Adsorption

In the foregoing, only molecular adsorption has been considered. However, some molecules (e.g. H_2, CO) can dissociate upon adsorption and, hence, two sites are required. Consider the dissociative adsorption equilibrium of hydrogen:

$H_2 + 2\,{}^* \leftrightarrow 2H\,{}^*$

In an analogous way as in the preceding section for the molecular adsorption, the coverage with hydrogen atoms H follows (26) . The pressure dependency now follows the square root of the partial H_2 pressure at low coverage.

$$\theta_H = \frac{\sqrt{K_{H_2} p_{H_2}}}{1 + \sqrt{K_{H_2} p_{H_2}}}$$ …………………(26)

Temperature and Pressure Dependence

Typical behavior can be expected with respect to the temperature dependence of catalyzed reactions, due to the effect of (competitive) adsorption. This will be demonstrated with some simplified cases of the reaction A ↔B, starting with a consideration of the rate determining step.

Transition –State Theory

According to the transition – state theory molecules react through unstable intermediates called transition –state complexes which then react to products. For instance, the surface reaction A* ↔B*, which is considered to be the rate –determining step, proceed s as follows:

$${}^*A \underset{k_-^\#}{\overset{k_+^\#}{\rightleftarrows}} {}^*A^\# \xrightarrow{k_{\text{barrier}}} {}^*B$$

It is assumed that the reacting complex(A*) is in equilibrium with the transition –state complex (*$A^{\#}$), and that the number of molecules in the transition state that react to the product (*B) per unit of time is given by the frequency k_{barrier} .This latter step is assumed to be rate limiting . The reaction rate constant can then be computed from expression (27).

$$k = k_{\text{barrier}} \left(\frac{k_{+}^{\#}}{k_{-}^{\#}} \right) = k_{\text{barrier}} K^{\#} \qquad \text{……….(27)}$$

Expression (27) is valid when energy exchange is fast compared to the overall reaction rate. Since $k^{\#}$ is an equilibrium constant, it can be written as in Eqn. (28) , where $\Delta G^{\#}$,$\Delta H^{\#}$ and $\Delta S^{\#}$ are the Gibbs free energy , the enthalpy and the entropy differences between the transition state and the ground state, respectively.

$$K^{\#} = \exp\left(\frac{-\Delta G^{\#}}{RT} \right) = \exp\left(\frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \right) \qquad \text{…….(28)}$$

As long as quantum –mechanical corrections can be ignored, the rate of reaction of the transition –state complex is the same for all reactions and is given by Eqn. (29).

$$k_{\text{barrier}} = \frac{k_B T}{h} \qquad \text{………………..(29)}$$

Where K_B is the Boltzmann constant and h is plank's constant. k_{barrier} is typically 10^{12} s^{-1}

The overall rate constant then becomes

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \right) = A_0 \exp\left(\frac{-E_a}{RT} \right) \qquad \text{…………(30)}$$

$\Delta S^{\#}/R$ may be taken as a constant, because it only varies slightly with temperature. Furthermore, since the exponential term is so much more temperature –sensitive than the pre-exponential term k_o, this latter term may also be taken as a constant ,resulting in the second equality of Eqn (30).

$\Delta H^{\#}$ can be identified with the activation energy Ea (neglecting a contribution of RT) of the reaction in fig . (6), ΔH represent s the reaction enthalpy for the reaction A* → B* . More detailed treatments are presented by Maatman (44) , Boudart , and Djega – Mariadassou (43) , and Van santen and Niemantsverdriet (45) .

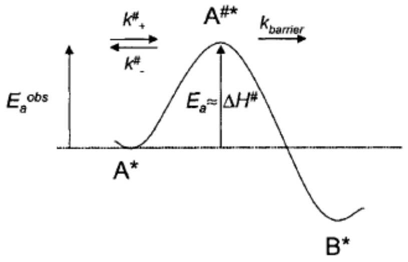

Figure 6: Energy diagram for a surface reaction .

Forward Reaction – Temperature and Pressure Dependence

For the conversion A↔B, the overall activation energy is a complex function of the reaction enthalpies and activation energies of the individual elementary reaction steps .We will this by assuming that the surface reaction is the rate –determining step (17) and that the backward reaction can be neglected . The rate expression for this single –site reaction can now be written as

$$r = \frac{k_2 N_T K_A p_A}{1 + K_A p_A + K_B p_B}$$ ……..(31)

Where $k_A = k_1$ and $K_B = 1/k3$.

The dependence of the reaction rate (34) on pressure and temperature is determined by contribution of both the numerator and denominator. Often, rate expression are presented in a power law form :

$$r = kp_A^{n_A} p_B^{n_B}$$ ……..(32)

Comparison with Eqn. (31) suggests that the powers n_A and n_B will not be constants .They can be extracted as follows :

$$n_i = \frac{\partial \ln r}{\partial \ln p_i}$$ ………….(33)

Applying Eqns. (31) to (33) ,and using the adsorption equilibrium relationships (Eqns, (14), and (15)) ,together with Eqn.(16),yields :

$$n_A = 1 - \theta_A \qquad \text{and} \qquad n_B = -\theta_B$$ ………………..(34)

Hence, the apparent reaction orders are related to the fractional surface coverages. From Eqn. (34),it follows that n_A varies from 0 to 1 ,and n_B from -1 to 0 , depending on the conditions.

Like the pressure dependence, the temperature dependence is also often expressed in an empirical form, in which an apparent overall rate constant is used (like in Eqn. (30). The observed (or apparent) activation energy can be expressed as :

$$E_a^{obs} = RT^2 \left(\frac{\partial \ln r}{\partial T} \right)_p$$ ……………(35)

The observed activation energy can now be derived from Eqn. (31) in a similar way as the derivation of the reaction powers as a function of surface coverage:

$$E_a^{obs} = E_{a2} + (1 - \theta_A)\Delta H_A - \theta_B \Delta H_B$$ ………………..(36)

The observed activation energy contains contributions from the rate –determining step (Ea2) and from the adsorption enthalpies of A and B , the latter depending on the fractional occupancies. Obviously, E a^{obv} will depend on the experimental conditions. Therefore, it is not surprising that a wide range of values have been reported for the same reaction system.

Forward Reaction –Limiting cases

Based on the previous analysis of the pressure and temperature dependence of the reaction order and the observed activation energy, four different cases can be distinguished

Strong Adsorption of A

Strong adsorption of A results in $k_A p_A$ >>1 and $k_B p_B$,and hence Eqn.(31) reduced to :

$$r = k_2 N_T$$ ……(37)

Physically this means that the whole catalyst surface is covered with A ($\theta_A \rightarrow 1, \theta_B \rightarrow 0$) .

Therefore, varying the partial pressure of A does not influence the reaction rate. The reaction is said to be zero order in A (and B) . The overall activation energy is E a^{obv} =Ea2, provided the concentration of active sites N_T is temperature independent .

Weak Adsorption of A and B

When A and B are only weakly adsorbed , $k_A p_A$ and $k_B p_B$ << 1 and θ_A ,θ_B → 0, so the rate expression becomes :

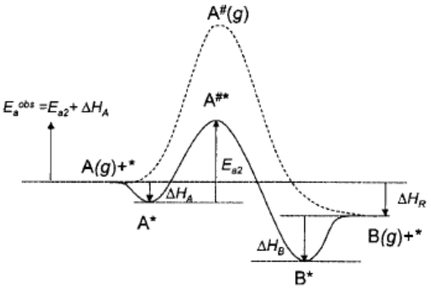

Figure 7: Energy diagram for the catalytic conversion of A to B . * denotes surface vacancy and # transition state . ΔH R is the reaction enthalpy . Included is the energy diagram for the phase conversion (dashed curve).

$$r = k_2 \, N_T \, K_A \, p_A \qquad \text{……………(38)}$$

The reaction is now first order in A and zero order in B . The observed overall activation energy will be lower than in previous case .

$$E_a^{obs} = E_{a2} + \Delta H_A \qquad \text{……..(39)}$$

Since the enthalpy of adsorption of A, is negative; adsorption is an exothermic process. This result can be understood from the energy diagram in fig. (5). Due to the low occupancy of A, for reaction to occur, adsorption of gaseous A is required, and hence A gains adsorption enthalpy. Subsequent surface reaction requires overcoming the activation energy.

Strong Adsorption of B

In this case $k_B p_B$ >> 1 and $k_A p_A$,and $\theta_A \rightarrow 0$, $\theta_B \rightarrow 1$, and the rate expression becomes :

$$r = \frac{k_2 N_T K_A \, p_A}{K_B \, p_B} \qquad \text{……………..(40)}$$

The reaction is first order in A and -1 in B (B decreases the reaction rate strongly by competitive adsorption). The surface is nearly completely covered with B. Therefore, the initial state for the reaction is gaseous A and adsorbed B (Fig 8). For A being able to react ,firstly a molecule of B must desorb with accompanying desorption enthalpy , and reacts through the surface reaction ,where the activation energy barrier has to be overcome . Thus, the observed activation energy is higher than in the previous cases

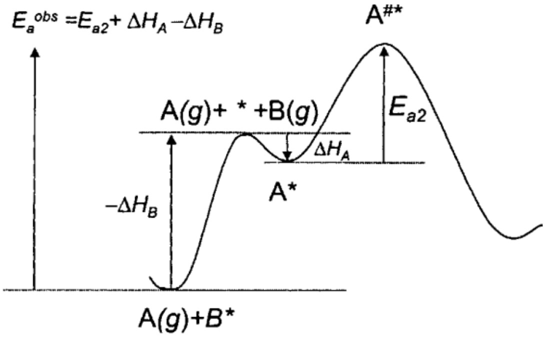

Figure 8: Energy diagram for the catalyzed conversion of A to B in the case of strong adsorption of B.

$$E_a^{obs} = E_{a2} + \Delta H_A - \Delta H_B \quad \text{……….(41)}$$

Note that $-\Delta H_B > -\Delta H_A$ a consequence of the stronger adsorption of B.

CONCLUSION

The preceding sections indicate how useful approximate reaction rate expression can be derived for catalyzed reactions, starting from an assumed kinetic model of elementary reaction steps. The derivation is based on the following assumption:

- The reaction system is in a steady –state.
- The surface for adsorption and reaction is uniform .
- The number of active sites is constant, independent of reaction conditions.
- Adsorption species do not interact, a part from their reaction paths.

The steady –state approach generally yields complex rate expression. A simplification is obtained by the introduction of one or several rate- determining steps and quasi-equilibrium steps, and further by the initial reaction rate approach. For complex reaction schemes, identifying the most abundant reaction intermediate s and making use of the site balance can simplify the kinetic models and rate expressions .

An interesting further development in describing the kinetics of heterogeneously catalyzed reactions is the so-called microkinetic approach ,whereby independent information about adsorbed species from temperature programmed desorption and spectroscopic studies are used to predetermine rate and equilibrium constants of elementary processes . thus enabling the prediction of the overall rate. Especially for metal catalyzed reactions this gives good results.

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