

Modern Heterogeneous Catalysis

An Introduction

Rutger A. van Santen

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The Author

Prof. Dr. Rutger A. van Santen
Eindhoven University of Technology
Faculty of Chemistry and Chemical
Engineering
Institute of Complex Molecular Systems
Den Dolech 2
5600MB Eindhoven
The Netherlands

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Chapter 3

Physical Chemistry, Elementary Kinetics

3.1 Introduction

A heterogeneous catalyst typically consists of millimeter-sized particles that are prepared in a specific shape that controls their strength. These particles are packed or circulated in a reactor bed with a dimension of centimeters in laboratory experiments, or with a dimension of a meter or more in industrial systems. Small particles of metal or other catalytically active materials are distributed on high surface area porous supports, so that the maximum amount of material is available for reaction.

The different characteristic dimensions of the catalytic reactor bed are illustrated in [Figure 3.1](#).

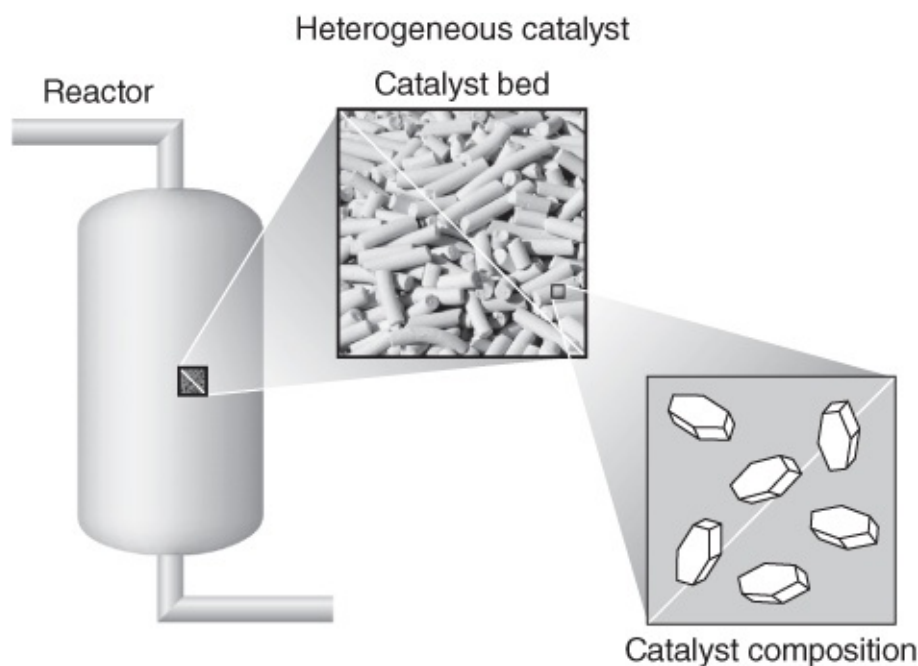


Figure 3.1 The relative dimensions of catalytic process components; reactor(meters), catalyst particle(millimeters), catalytically active components(microns or less).

Hydrodynamics determines the flow properties in the reactor that has a process time that can vary from minutes to hours. Within the catalyst particles, the flow is subject to diffusional resistance, which depends on the length and distribution of the particle pore sizes. The dimensions of these micropores can vary in size from a micron to several nanometers. The catalyst particle can also be an aggregate of crystallites, such as a zeolitic system with smaller micropores on the order of a nanometer. These crystallites are often embedded in an amorphous material to give the large catalyst particles their strength.

The catalytically reactive nanoparticles distributed on the surface of the porous catalyst

particle can vary significantly in size as well as location and this distribution can have a large impact on the overall catalyst reactivity. The reactivity of the active particles depends on their size and shape, but due to the effects of diffusion, their contribution to overall catalysis will also depend on their position in the pore structure.

Ultimately, the chemical reactivity of the catalytic particle is determined by the atomistic structure of the catalytically reactive centers on that particle.

The early discoveries in heterogeneous catalysis during the previous century were accomplished without a scientific framework of the understanding of surface chemistry and reactivity at a molecular level. The content of this book, which is written a century later, describes the current deep understanding of the molecular basis of heterogeneous catalyst reactivity. This is described in detail in Part II. This chapter serves as an introduction to the basic physical chemical and kinetic concepts that will provide a context for the later chapters on mechanism and catalytic modeling.

Operation of a catalytic reactor depends not only on the chemical process of catalysis, but also on the processes of mass and heat transfer. These processes are determined by physical properties such as catalyst particle size, pore volume and distribution, and internal surface area as well as the stoichiometry of the catalyst's composition. Since it has been possible to measure these properties since the beginning of catalytic science in the previous century, they were the earliest parameters to be related to catalyst performance.

The scientific basis of mass or heat transfer limitations of the catalyst particles and the consequences of these limitations for reactor design was formulated in the middle of the last century, and this has evolved into the important discipline of chemical reaction engineering [1, 2]. In parallel, kinetics also developed into an important branch of physical chemistry. The measurement of the rate of reaction as a function of partial pressures of the reactant and product became an important tool for deducing information on rate-controlling steps, and for correlating catalyst performance with catalyst composition and physical structure [3].

A reaction mechanism can never be firmly established based solely on overall kinetics measurements because too many molecular reactivity parameters are unknown. This process has been enhanced by the recent availability of molecular reactivity information from computation and surface science data. The phenomenological development of catalyst kinetics became an important tool for analyzing catalyst performance, for estimating reactor requirements, and for optimizing process design. Complemented by chemical thermodynamics, the determination of reaction mechanisms became essential to reactor modeling and also provided important inputs for the improvement of catalytically active materials.

In order to predict which material is optimum for a catalytic reaction, we need to know how catalyst performance relates to catalyst composition and structure. Therefore, the characterization of the structure of a catalyst at various scales relevant to catalytic operations is a core activity of heterogeneous catalysis science.

In the early twentieth century, quantitative product determination was difficult due to the

complexity of product analysis. Now, with new tools for physical analysis and with modern test facilities, this can be done almost automatically on a laboratory scale.

Determining catalyst structure and composition on a molecular level still presents a significant challenge because the complexity of the catalytic system makes complete molecular characterization difficult. Synthesis control on a molecularly defined level presents a similar challenge. Therefore, empirical exploration remains essential to catalyst research. There is ample scope for further refinement of the techniques for catalyst characterization and synthesis.

The ultimate difficulty in the search for an optimum catalyst is that reactivity is controlled on a molecular level by the topology of the atoms that constitute a catalyst's surface site. Catalyst preparation affords full molecular control and complete atomistic characterization only in the rare case when model molecular catalytic systems are used. [Figure 3.2](#) shows an example of such a catalyst with an Ir₄ cluster prepared by immobilizing the corresponding carbonyl complex on the internal aluminosilicate surface of a zeolite.

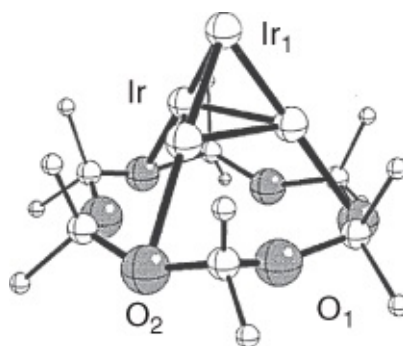


Figure 3.2 Ir₄ cluster supported on the zeolite fragment Al₃Si₃O₆H₁₂³⁻. (Ferrari *et al.* 2008 [4]. Reproduced with permission of American Chemical Society.)

Conventional heterogeneous catalysts are inhomogeneous, and the molecular character of the optimum reaction center is often not known. An additional complication is that the catalyst surface often reorganizes during reaction. As we will see in [Chapter 4](#), this reorganization may initially activate the catalyst, but will ultimately lead to its deactivation. Advanced spectroscopic techniques that can be applied *ex situ* as well as *in situ* (*in operando*) are available to unravel the complex chemical constitution of the working catalyst.

Due to the inhomogeneous nature of the catalysts, model catalyst studies based on the techniques of surface science [5, 6] have been very useful, because model catalytic systems are more homogeneous and allow for detailed atomistic characterization of the catalytically active system. Examples of the single crystal surfaces of transition metals used in such experiments are shown in [Figure 3.3](#).

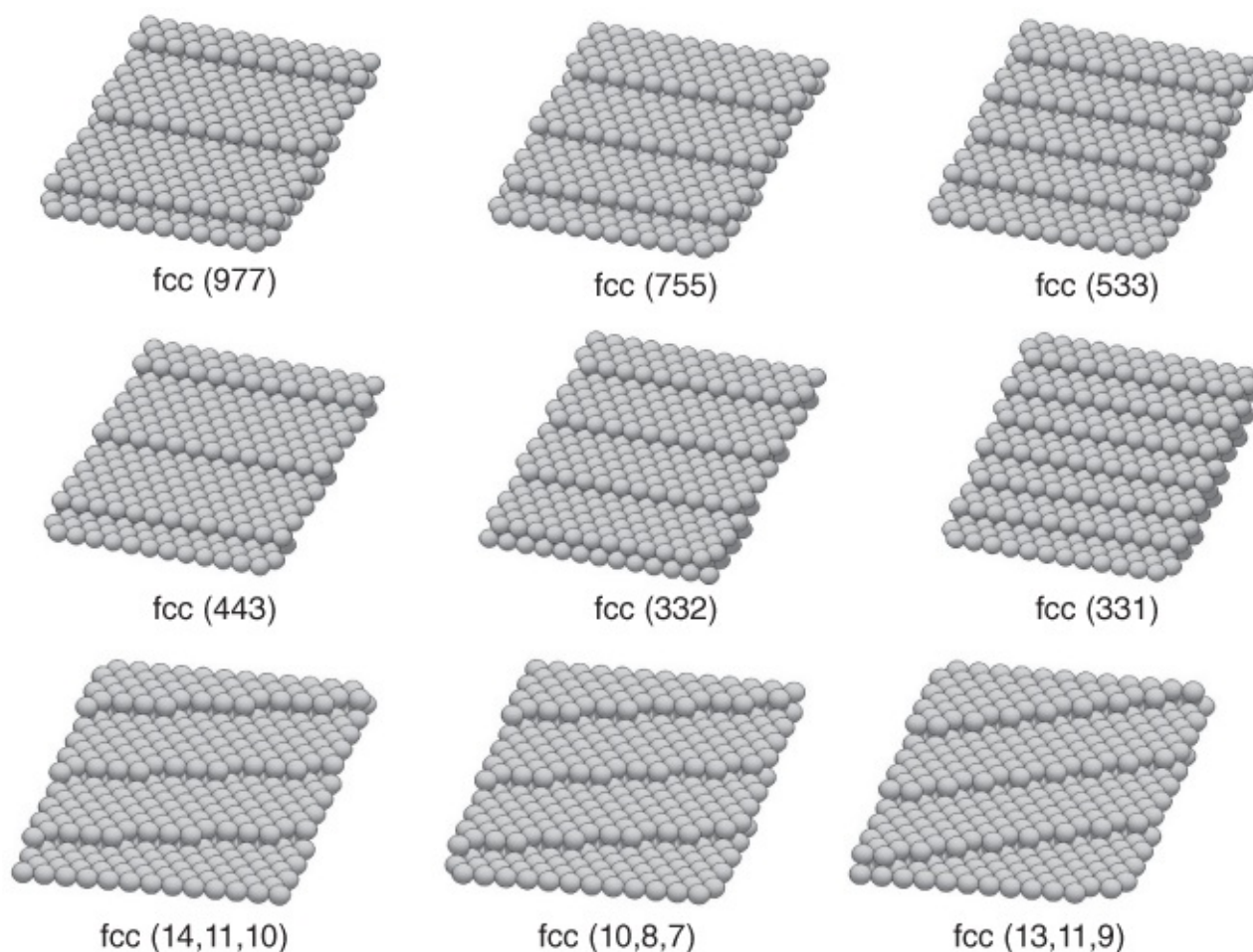


Figure 3.3 Schematic representation of the surface structures of several stepped (first two rows) and kinked (bottom row) crystal faces deduced from the bulk unit cell of a face-centered cubic crystal. The numbers within the brackets denote crystallographic directions. The non-stepped surface is the (111) surface, with each surface atom having six neighbor atoms in the plane and three below the plane. Contraction of interlayer spacing and other modes of restructuring that are commonly observed are not shown. (Somorjai and Li 2010 [7]. Reproduced with permission of John Wiley & Sons.)

Computational quantum-chemical approaches such as density functional theory (DFT) [8] have reached a high level of maturity and are now the basis of computational catalysis. This approach is very useful for simulating the reactivity of realistic models of catalytically reactive centers at a molecular level [8–10]. These types of calculations are used to study the relative stability of reaction intermediates and are indispensable for microkinetic simulations. The resulting detailed scientific understanding of the relationship of molecular surface chemical reactivity to catalyst surface composition and structure has a great influence on our predictive abilities.

Computational chemistry and physics provide important tools to analyze the atomistic structure of catalytically reactive sites by comparing calculated spectra to measured spectra [10, 11].

Section 3.2 briefly describes some of the most important techniques for characterizing

heterogeneous catalysts. In [Section 3.3](#), we will present the fundamental kinetics equations and elementary rate equations used in heterogeneous catalytic kinetics, and explain the design of the Sabatier volcano curve. [Section 3.4](#) will introduce transient kinetics methods that are useful to unravel the elementary rate constants of the overall catalytic reaction cycle, and also to determine the fraction of reactive surface centers. The final section considers diffusion and its interplay with kinetics.

3.2 Catalyst Characterization

A heterogeneous catalyst typically consists of a high surface area inert support on which small catalytically active particles have been distributed. The smaller the catalytically reactive particles, the more efficient the process, because small size maximizes the number of particle atoms that are exposed. The high surface area of the inert support allows for a high density of the small catalytically active particles in a finite volume. The support is also needed to stabilize the particles against particle growth, so that they remain small. Most often the “inert” high surface area support is an oxide that has some innate reactivity. If this reactivity is not beneficial, promoters or moderating compounds are used to suppress it. A challenge in catalyst synthesis lies in the ability to prepare catalysts with uniform particle size and well-defined pore structure. Since this is often not achieved, a significant goal of catalyst research is to understand this inhomogeneity and the actual composition of the heterogeneous catalyst.

Catalyst performance characterization involves determining the kinetics properties of the catalytic reaction as well as the physical characterization of the catalyst.

In the laboratory, catalyst performance is measured in microreactors as shown in [Figure 3.4](#). (For an introduction to the chemical reactor engineering of such reactors refer to Levenspiel [1].) These catalyst test reactors require only a few grams of catalyst, and can be operated isothermally, without internal pressure or flow gradients when the catalyst particle dimensions, flow conditions, and reactor size are chosen properly [13]. Most of the kinetics data discussed in this book have been obtained from such measurements.

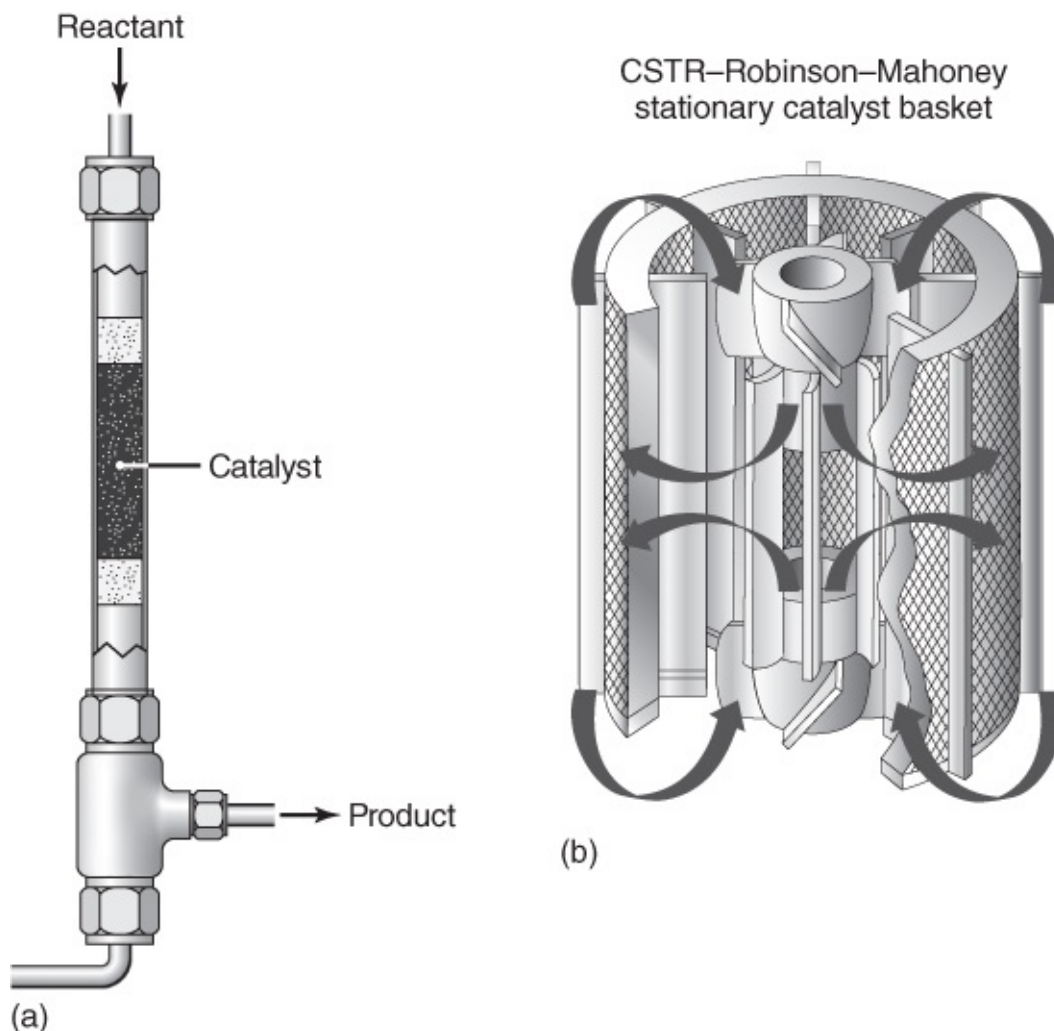


Figure 3.4 (a) Plug flow micro reactor. (b) Continuous stirred tank reactor (CSTR) [12].

The four essential questions for catalyst characterization are as follows:

1. What is the surface area and porosity of the catalyst?
2. What is the composition of the catalytically reactive particles, and what is their size and shape distribution?
3. What fraction of the exposed surface contains the catalytically reactive centers?
4. What is the state of the catalyst at reaction conditions?

While the first two questions can be answered by studying the catalyst before and after the reaction, the third and fourth require a characterization study of the catalyst while it is in operation.

Volumetric adsorption methods are fundamental to heterogeneous catalyst characterization. They are based on the chemisorption of molecules on a reactive surface or on the physical adsorption of molecules on the entire catalyst surface. Chemisorbing molecules form chemical bonds with a surface which is material-specific. Physical adsorption is due to weak dispersion or van der Waals interaction between adsorbate and surface, and is not material-specific. This property can also be used to determine the pore volume of the catalyst.

3.2.1 Langmuir Adsorption Isotherm

A classical expression used in chemisorption is the Langmuir's adsorption isotherm (Eq. (3.1)), which computes the surface coverage as a function of gas pressure and size of adsorbing molecule. This expression is also important in kinetics modeling studies. By measuring the change in gas pressure, the amount of gas adsorbed can be deduced, and the surface area and equilibrium adsorption constant can be determined:

$$\theta = \frac{K_{eq} \frac{P}{P_0}}{1 + K_{eq} \frac{P}{P_0}} \quad 3.1$$

In Eq. (3.1), θ is the fraction of surface sites occupied by the adsorbing gas, P is gas pressure, P_0 is the pressure of gas at standard temperature and pressure conditions, and K_{eq} is the equilibrium constant of adsorption defined as the ratio of the rate constant of adsorption k_{ads} , and the rate constant of desorption k_{des} . θ is determined by using the surface area of the adsorbing gas as a unit measure of material.

Langmuir's view of a surface is analogous to a checkerboard surface like the terraced surfaces in Figure 3.3 without the step-edges. Equation (3.1) is valid as long as one molecule adsorbs per site, the number of sites is finite, the sites are identical, and the adsorbing molecules do not interact. The characteristic of Langmuir adsorption is its initial linear dependencies of surface coverage on gas pressure (Henry's law) and on the saturation of surface coverage at higher pressure, which is due to the finite number of adsorption sites (see Figure 3.5). The Langmuir adsorption isotherm for adsorption of a non-dissociating molecule is deduced from equilibration of rates of adsorption $\vec{v}_{ads}$ and desorption $\overleftarrow{v}_{des}$ respectively:

$$\begin{aligned} \vec{v}_{ads} &= \overleftarrow{v}_{des} \Rightarrow k_{ads} \frac{P}{P_0} (1 - \theta) N_s = k_{des} \theta N_s \\ \Rightarrow \frac{\theta}{1 - \theta} &= \frac{k_{ads} \frac{P}{P_0}}{k_{des}} = K_{eq} \frac{P}{P_0} \end{aligned}$$

N_s is the total number of sites, θ is surface coverage, k is the rate of adsorption and desorption, P is pressure, and P_0 is the pressure at STP (Standard Temperature and Pressure).

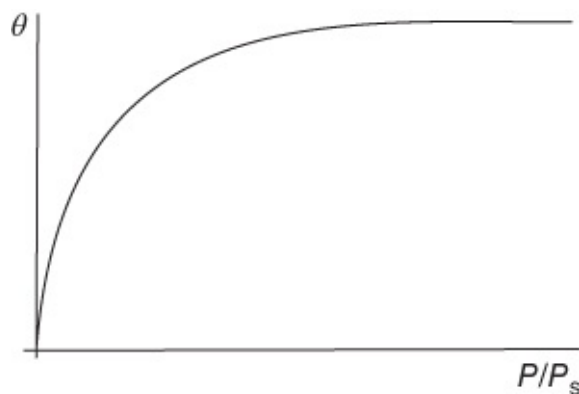


Figure 3.5 Langmuir adsorption isotherm; Coverage θ as a function of pressure. θ saturates at high pressure.

The volumetric adsorption of reactive gasses that dissociate, such as CO or H₂, can be used to measure the surface area of catalytically reactive particles. In later chapters we will discuss the questionable nature of the assumptions of identical sites and the absence of lateral interactions. Nonetheless, the expression in Eq. (3.1) is very useful and is widely used to deduce free energies of adsorption.

3.2.2 Measurement of Pore Volume

At the time of its discovery, the BET (Brunauer, Emmet, Teller) [14] expression based on physical adsorption represented a breakthrough for determining the total surface area and pore volume of a catalyst. The BET equation uses the change in pressure at a temperature close to gas condensation.

As long as the pressure of the gas is below the condensation pressure, Langmuir-type adsorption will occur over the entire surface, but when pressure increases, condensation will occur instead of adsorption saturation.

The BET adsorption isotherm is given by Eq. (3.2).

$$\frac{P}{V_{\text{ads}}(P_s - P)} = \frac{1}{CV_m} + \frac{C - 1}{CV_m} \frac{P}{P_s} \quad 3.2$$

V_{ads} is the volume of gas adsorbed and V_m is the volume per molecule. P_s is the saturation pressure at the condensation temperature of gas. From the plot of volume of gas adsorbed V_{ads} versus P/P_s from Eq. (3.2), the monolayer volume of gas V_m that can be adsorbed can be deduced and, since the surface area of the molecule is known, will give the total surface area of the entire catalyst particle. C is defined in Insert 3.1, that gives the derivation of the BET equation in Insert 3.1.

Insert 1 Multilayer Adsorption; the BET Equation

As in the derivation of the Langmuir adsorption, we will equilibrate the rates of adsorption and desorption, but since we have to consider condensation, subsequent layers on top of each other have to be considered (after [3]):

$$\text{Layer 1} \rightarrow r_0^{\text{ads}} \theta_0 = r_0^{\text{des}} \theta_1; r_0^{\text{ads}} = k_0^{\text{ads}} \frac{P}{P_s}$$

$$\text{Layer 2} \rightarrow r_1^{\text{ads}} \theta_1 = r_1^{\text{des}} \theta_2; r_1^{\text{ads}} = k_1^{\text{ads}} \frac{P}{P_s}$$

In the second and following layers, molecules only absorb on previously absorbed molecules. Now, assume that all $r_i (i \neq 0) = r_1$. At condensation pressure $P = P_0$:

$$r_1^{\text{des}} = r_{\text{evap}} = r_{\text{cond}} = k_1^{\text{ads}} \text{ and } r_1^{\text{ads}} = r_{\text{cond}} \frac{P}{P_s}$$

Hence

$$\frac{\theta_2}{\theta_1} = \frac{r_1^{\text{ads}}}{r_1^{\text{des}}} = \frac{r_{\text{cond}} \frac{P}{P_s}}{r_{1,\text{evap}}}$$

and

$$\frac{\theta_2}{\theta_1} = \frac{P}{P_s} = x \Rightarrow \theta_i = x^{i-1} \theta_1$$

$$\frac{\theta_1}{\theta_0} = \frac{k_0^{\text{ads}} \frac{P}{P_s}}{r_0^{\text{des}}} \Rightarrow \theta_i = C x^i \theta_0 \left(C = \frac{k_0^{\text{ads}}}{r_0^{\text{des}}} = K_{\text{ads}}^0 \right)$$

The total number of molecules adsorbed per unit surface area n_t is

$$n_t = \sum_{i=1}^{\infty} i \theta_i = C \theta_0 \sum_{i=1}^{\infty} i x^i.$$

Conservation of number of sites gives: $1 = \theta_0 + \sum_{i=1}^{\infty} \theta_i = \theta_0 \left(1 + C \sum_{i=1}^{\infty} x^i \right)$ with

$\sum_{i=1}^{\infty} x^i \approx \frac{x}{1-x}$ ($x < 1$) and $\sum_{i=1}^{\infty} i x^i = \frac{x}{1-x^2}$ gives $n_t = \frac{Cx}{(1-x)(1-x+Cx)}$ that can be written as Eq. (3.2).

3.2.3 Porosity

In [Figure 3.6](#), a characteristic adsorption isotherm is shown for N₂ adsorption on a high surface area η -alumina.

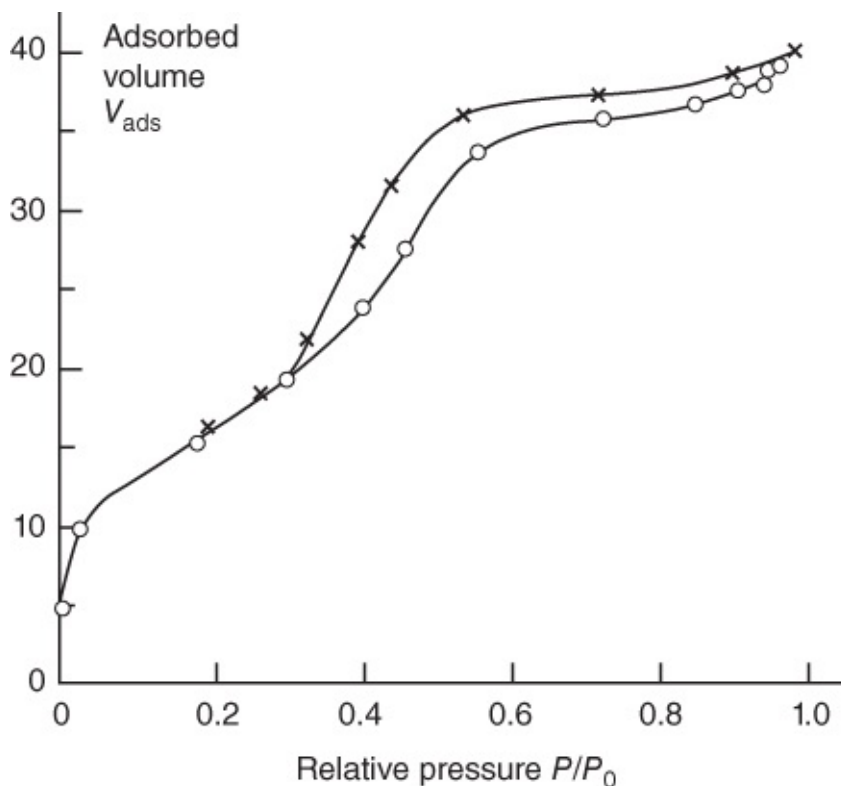


Figure 3.6 Adsorption of N₂ at 77.3 K on η -alumina. ○ = increasing pressures and × = decreasing pressures. (After [3].)

In addition to the increasing multilayer adsorption of N₂, [Figure 3.6](#) illustrates that at even higher temperatures hysteresis occurs in the adsorption behavior so that the amount of liquid adsorbed varies when pressure increases or decreases. This hysteresis relates to the capillary forces that arise when liquid condenses into the mesopores ($2 \text{ nm} < d < 50 \text{ nm}$) of the catalyst particles. Hysteresis occurs due to the non-uniformity of the pores. In this case, we refer to the Kelvin equation:

$$P_K = P \exp \left(\frac{-2\gamma V}{r_b RT} \right) \quad 3.3$$

P_K is the equilibrium pressure of the liquid in the pore, P is the equilibrium pressure of the free liquid, γ is the surface tension of the fluid, r_b is the capillary radius, R is the gas constant, and T and V are the temperature and the volume of the liquid.

A pore with a small neck radius will fill at relatively low pressure, but it will only completely fill at the higher pressure consistent with its larger body radius. For desorption to occur, the pressure must initially be low enough to cause evaporation of the liquid at the bottleneck.

The hysteresis loops of physical adsorption isotherms can be used to deduce the dimensions and shapes of the capillaries in the catalyst particles. These are called ***T-plots***, and their

values can also be obtained by measuring the physical adsorption of non-reactive gas molecules such as N₂ or noble gas molecules [11].

3.2.4 Temperature-Programmed Reactivity Measurements

Temperature-programmed reduction (TPR) or temperature-programmed oxidation (TPO) experiments can be used to determine the weight loss or increase of the total amount of reactive material. Reduction uses H₂ uptake as a function of temperature, while oxidation uses oxygen consumption as a function of temperature. Instead of measuring chemisorption, which is a surface measurement, TPR experiments measure the bulk reactivity properties of a particular reactive material. These measurements are element-specific because the temperatures of oxidation or reduction will depend on the material studied. Additionally, temperatures can be varied with particle size and can thus be used as an indicator of reactive particle sizes. As we will discuss in [Chapter 11](#), smaller metal-oxide particles tend to reduce at higher temperatures.

3.2.5 Spectroscopic Techniques

The evolution of catalyst characterization has involved the use of spectroscopy for collecting data of increasing detail at the molecular level. Some important spectroscopic techniques are listed:

- *Electron microscopy* can determine the particle size distribution of the catalytically reactive particles on the catalyst at the nano- and micron levels. High resolution studies reveal atomistic-level details of the catalyst.
- *X-Ray photo emission spectroscopy (XPS)* enables identification of low concentration elements on the surface of catalyst materials based on the energy of emitted electrons.
- *Extended X-ray absorption fine structure (EXAFS) spectroscopy* is used at synchrotron facilities to measure the local coordination of atoms that are part of the partially disordered materials of a reactive catalyst.
- *Infrared and Raman spectroscopies* are vibrational spectroscopies useful for probing the interaction of adsorbed molecules with catalyst surfaces. Changes in bond frequencies provide information on the activation of molecules by reactive substrates.

For a detailed discussion of these techniques, see [11, 15].

Methods for bulk solid-state characterization such as X-ray diffraction and solid-state nuclear magnetic resonance (NMR) are also widely used. X-ray diffraction can not only determine the structure of compounds that constitute the catalyst, but can also be used to measure particle size. In addition, to assist structure determination, solid-state NMR spectroscopy can also be used to probe the state and mobility of adsorbed molecules in microporous systems such as the zeolites [16].

While most physical characterization is conducted on catalyst particles before or after a reaction, there is an increasing interest in the development of methods to study the catalyst

surface during the catalytic reaction. This is achieved by combining spectroscopies that can be applied in an ambient environment with catalyst reaction measurements [17].

3.3 Elementary Kinetics

3.3.1 Lumped Kinetics Expressions: Kinetic Determination of Key Reaction Intermediates

Knowledge of the kinetics of a reaction enables to calculate the rate of reaction as a function of reaction concentration and temperature. The kinetics of a reaction is based on a proposed mechanistic model. For a catalytic reaction, this will be a cyclic sequence of sometimes competing elementary reaction steps.

3.3.1.1 The Rate Constant of an Elementary Reaction

The elementary reaction is defined as a single chemical bond-breaking or formation event that connects the local equilibrium state of the initial reacting intermediate(s) with the next new reaction intermediate that is again in a local equilibrium state. The probability of progressing from one equilibrium state to the next for this particular transformation is the rate constant of the elementary reaction. It is given by Eyrings' transition state reaction rate expression [18]:

$$r_T = \frac{kT}{h} \exp\left(-\frac{\Delta G^\ddagger}{kT}\right) \quad 3.4$$

r_T is the rate constant, k is the Boltzmann constant, and h is the Planck constant. $\Delta G^\ddagger$ is the activation-free energy of the reaction. This is an Arrhenius-type expression that depends exponentially on an energy divided by the temperature T . kT/h is a frequency of the order of 10^{13} per second. The reaction rate expression in Eq. (3.4) relates the reaction rate of the elementary reaction step to the free energy difference between the transition state and the ground state. The transition state is defined as the minimum free energy saddle point on the potential energy surface that connects the two reaction intermediate equilibrium states, which are the initial and final states of the elementary reaction (see [Figure 3.7](#)).

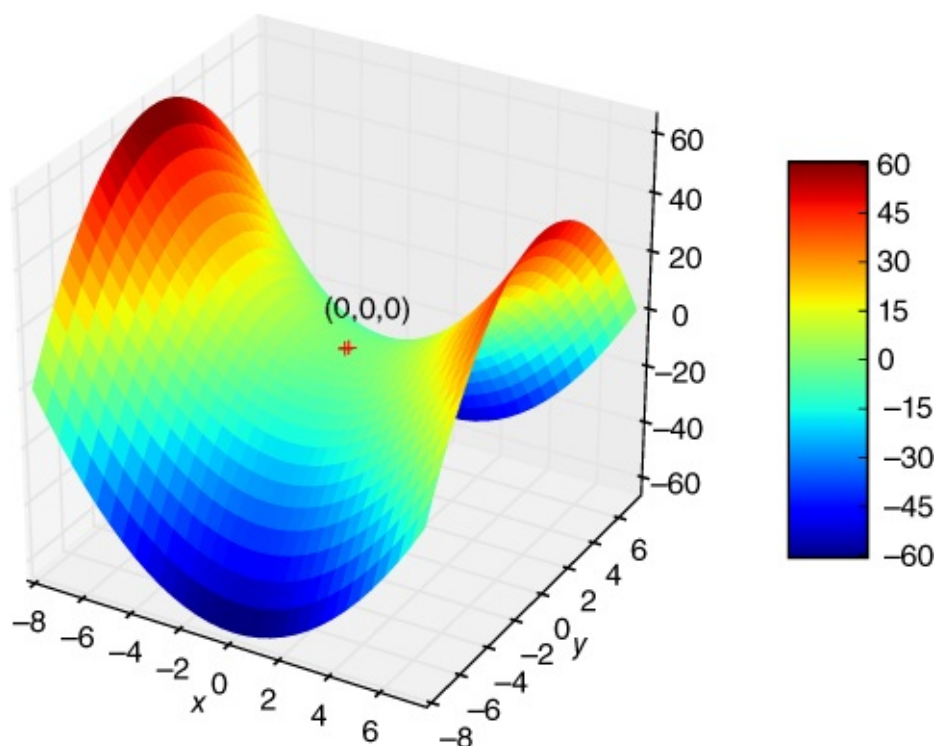


Figure 3.7 Potential energy saddle point diagram illustrating the relationship between transition state, reactant, and product state. The local energy minima ($x = 0$, $y = -8$ and $x = 0$, $y = 6$) indicate reactant and product state respectively. The potential energy saddle point ($x = 0$, $y = 0$) defines the transition state.

The Eyring transition state rate expression of an elementary reaction is based on the essential assumption that reaction probability is slow compared to the rates of energy exchange between the reacting system and its environment. This is valid as long as (and because) the activation energies of a bond formation or bond cleavage are usually higher than 5 kT . The transition state can be considered in equilibrium with the equilibrium ground states. If this condition is not satisfied, as can be the case for surface diffusion, molecular dynamics approaches based on the solution of the Newton's equations must be used.

The second assumption is that once the system is in the transition state it moves to the other equilibrium state without probability of reflection. It implies that there is no friction due to high viscosity of a reaction medium.

Transition state theory requires the definition of a reaction coordinate q of the reacting system. This is one of the degrees of freedom of the system along which the bond cleavage or formation reaction takes place, and it is defined uniquely in the transition state. At the transition state, the second derivative of the energy with respect to the reaction coordinate is negative, whereas in the local energy minima it is always positive. In the transition state, all the other free energies of the reacting system are at their local energy minimum, except for the translational degrees or rotational degrees of freedom of a freely moving molecular system.

Eyring's reaction rate expression can be rewritten as Eq. (3.5).

$$r_T = v_T \exp \left(-\frac{E_{\text{act}}}{kT} \right) \quad 3.5$$

With:

$$v_T = e \frac{kT}{h} \exp \left(\frac{\Delta S^\#}{k} \right) \quad 3.6a$$

$$E_{\text{act}} = \Delta H^\# + kT \quad 3.6b$$

$$\Delta S^\# = \Delta S_{\text{transl}}^\# + \Delta S_{\text{rot}}^\# + \Delta S_{\text{vibr}}^\# \quad 3.6c$$

$$E_{\text{act}} = E_{\text{electr}}^\# + \frac{1}{2}h \left(\sum_{i=0}^N v_i^0 - \sum_{i=1}^N v_i \right) + kT \quad 3.6d$$

The activation energy of the reaction E_{act} (Eq. (3.6b)) is deduced from the expression in Eq. (3.4) by using its definition, which is the derivative of its logarithm with respect to $1/kT$ (for a more detailed discussion see [19], p. 138 and following). The pre-exponent v_T depends on the transition state entropy $\Delta S^\#$, and the activation energy E_{act} relates to the activation enthalpy $\Delta H^\#$, all of which are assumed to be independent of temperature. For a molecule that desorbs from the surface from an immobile adsorbed state, a typical value of v_T is 10^{17} ; for an adsorbing molecule it is 10^9 . This reflects the difference in mobility of the adsorbed molecule with respect to the gas phase. The activation entropy is a sum of the respective contributions of translational, rotational, or vibrational entropies (Eq. (3.6c)). These can be computed using statistical mechanics from the corresponding partition functions (see Insert 3.2). Within the harmonic approximation for the vibrational frequencies, the activation energy E_{act} can be deduced from quantum-chemical calculations using the expression Eq. (3.6d). $E_{\text{electr}}^\#$ is the electronic energy difference between the transition state and the ground state. v_i^0 and v_i are the frequencies of the equilibrium ground state vibrations and the frequencies of the vibrational modes of the transition state complex other than the reaction coordinate, respectively. N is the total number of vibrational nodes.

Insert 2 Statistical Mechanical Relations for Energy and Entropy

Once the partition function Q is known, thermodynamic properties can be calculated. The partition function Q is given by (after [20]):

$$Q = \sum_i \exp\left(-\frac{E_i}{kT}\right)$$

The energies E_i are the eigen energies of the system. From Q , the energy and entropy can be calculated from these relations:

$$E = kT^2 \frac{\partial}{\partial T} \ln Q$$

$$S = \frac{\partial}{\partial T}(kT \ln Q)$$

The partition function is the product of the respective partition functions of the degrees of freedom of the system.

$$Q = Q_{\text{trans}} \times Q_{\text{rot}} \times Q_{\text{vib}}$$

The expression of Q_{trans} for one degree of freedom is:

$$Q_{\text{trans}} = l \frac{(2\pi mkT)^{1/2}}{h}$$

m is the mass of the particle and l is the length of translation.

The expression for Q_{rot} of a linear molecule is:

$$Q_{\text{rot}} = \frac{8\pi^2 IkT}{h^2}$$

I is the momentum of inertia.

The expression for the contribution of one vibrational degree of freedom within the harmonic approximation is:

$$Q_{\text{vib}} = \frac{e^{-\frac{1}{2} \frac{h\nu}{kT}}}{1 - e^{-\frac{1}{2} \frac{h\nu}{kT}}}$$

When activation entropies are calculated instead, the following expression is used:

$$Q'_{\text{vib}} = \frac{1}{1 - \exp\left(-\frac{h\nu}{kT}\right)}$$

The zero-point vibrational energy correction $\frac{1}{2}h\nu$ has been incorporated into the activation energy expression calculated from the electronic energy.

The electronically calculated saddle point energy is to be corrected with the zero-point frequencies of all ground state degrees of freedom, except for the transition state vibrational frequencies of the non-reaction coordinate degrees of freedom. There is also a small correction to the activation energy barrier due to kT . Equations (3.5) is fundamental to the catalytic kinetics equations discussed in the next subsection.

3.3.1.2 Elementary Catalytic Reaction Kinetics

Because the catalytic reaction is a cycle that consists of a combination of elementary reaction steps, the energy reaction path and apparent activation energy have a complex relation with those same attributes of the elementary reactions that constitute the catalytic reaction cycle. This is the topic of this section.

The reaction step sequence that comprises a catalytic reaction cycle is called the ***mechanism of the reaction***. Since this sequence of elementary reactions is often unknown, one must propose a plausible mechanism.

A comparison of predicted kinetics with the measured kinetics of the reaction can be used to evaluate potential candidates. However, alternative mechanistic proposals can result in very similar kinetics, when elementary rate constant parameters are not known and are adjusted to correspond with the experiment. Without additional information, kinetic parameters obtained in this way are very helpful for catalytic reactor design, but are not sufficiently accurate to establish a conclusive relation between kinetic performance and catalyst chemical reactivity indicators.

This additional information can be deduced from *in situ* spectroscopic information about the surface composition of the working catalyst or from model chemical experiments, for instance those using isotope-labeled molecules (as discussed in [Section 3.4](#)). Quantum-chemical calculations on model systems can provide information on the relative stability of proposed reaction intermediates and activation energies of elementary reaction steps, and this aids considerably in the validation of a proposed reaction mechanism.

To calculate kinetics one must solve the set of kinetic equations for the rate of change of the reaction intermediates of the reaction. These are not only gas phase intermediate molecules that can readsorb, but are dominantly reaction intermediates adsorbed on the catalyst surface and only indirectly related to the reaction product. The kinetics equations are coupled ordinary differential equations (ODEs) that calculate product formation from the surface concentrations of these reaction intermediates. The equations are usually solved making the steady state assumption, so that the stationary rate of conversion to product is calculated.

In the elementary surface kinetics that we consider in this section, the Langmuir checkerboard surface model is used to build a kinetic model of a reaction. As in the Langmuir adsorption model, one type of surface site is considered and the adsorbing intermediates have no lateral interactions. The concentration of intermediates can be described by an average coverage θ_i . This corresponds to the mean field equation that assumes that the rate of surface diffusion is fast compared to the rate of the individual

elementary reaction steps, so surface concentrations can be considered to be uniformly distributed.

3.3.1.2.1 Site Number Conservation Law

The law of site number conservation states that the sum of the surface vacancy concentration and the surface coverages of reaction intermediates is equal to a constant.

$$\sum_i \theta_i + \theta_v = 1 \quad 3.7$$

θ_i is the surface concentration of intermediate i and θ_v is the surface vacancy concentration. It implies, as we will see, a fundamental difference between catalytic kinetics and non-catalytic kinetics. The latter assumes mass-action law kinetics, according to which the rate of a reaction is proportional to the product of the concentrations of reacting molecules.

Lumped kinetic expressions are often used in elementary kinetics. Every individual reaction step is not explicitly considered, but instead several steps may be contracted into one rate expression. This simplifies the equations to be solved as well as the interpretation of their results.

As an initial example, we will provide the solutions for the elementary lumped kinetics model of the formation of methane from synthesis gas. The mechanism of this reaction is shown by the reaction cycle in [Figure 3.8](#).

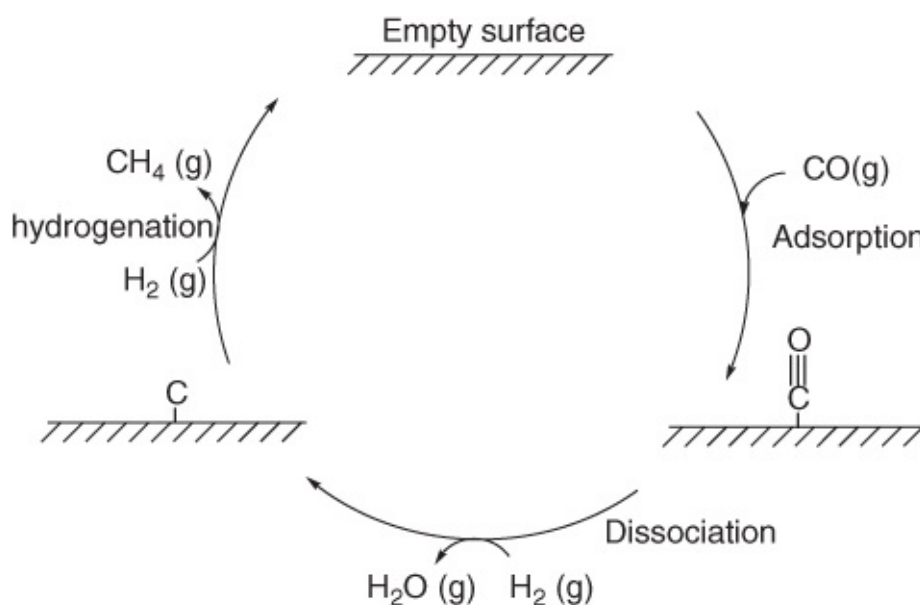


Figure 3.8 Lumped kinetics reaction cycle of methane formation from synthesis gas (schematic).

This lumped kinetics reaction cycle does not explicitly consider the dissociative adsorption of H_2 . Reaction is initiated by adsorption of CO and H_2 to empty surface sites, and the cycle closes with regeneration of empty surface sites by product desorption. θ_H is ignored because

this lumped kinetics reaction cycle does not explicitly consider dissociative adsorption of H₂.

The corresponding lumped kinetics equations are as follows:

$$R_{\text{CH}_4} = \frac{1}{N_s} \frac{d[P]}{dt} = k_H \theta_C \quad 3.8$$

Equation (3.8) gives the rate of product formation R from adsorbed C atoms. θ_C is the surface coverage of C. The rate constant k_H is the lumped reaction rate constant of C atom hydrogenation to methane. It implicitly depends on H₂ partial pressure.

$$\frac{d\theta_C}{dt} = k_{\text{diss}} \theta_{\text{CO}} (1 - \theta) - k_H \theta_C \quad 3.9a$$

$$\frac{d\theta_{\text{CO}}}{dt} = k_{\text{ads}}^{\text{CO}} \frac{P^{\text{CO}}}{P_0^{\text{CO}}} (1 - \theta) - k_{\text{des}}^{\text{CO}} \theta_{\text{CO}} - k_{\text{diss}} \theta_{\text{CO}} (1 - \theta) \quad 3.9b$$

$$\theta = \theta_C + \theta_{\text{CO}} \quad 3.9c$$

P^{CO} is the partial pressure of CO, P_0^{CO} is the partial pressure of CO at STP, and θ is the total surface coverage.

Equations (3.9a)–(3.9c) assume that the surface coverage by O atoms can also be ignored, which implies that the rate constant of their removal is fast compared to that of the other reactions. This assumption is useful for our illustrated example. It simplifies the ODEs since now only two surface species, CO and C, must be considered. The rate of C-atom formation is proportional to the reaction rate constant of CO dissociation k_{diss} and the product of θ_{CO} and surface vacancy concentration, since two atoms are generated by dissociation of CO and hence a vacant surface position next to the adsorbed position is required.

Conventionally, one proceeds to identify the rate-controlling step of the reaction. We will compare the cases where the rate constant of dissociation of adsorbed CO, k_{diss} , is large and the rate of C atom hydrogenation is fast, with the opposite case where k_{diss} is rate-controlling. By comparing the predicted and experimentally demonstrated partial pressure dependence, it can be established which of the two cases applies. This also indicates which reaction intermediate dominates the surface coverage.

Equations (3.9) can be solved within the steady state approximation ($d\theta_i/dt = 0$):

$$R_{\text{CH}_4} = \frac{k_H (1 - \theta_{\text{CO}})}{1 + \frac{k_H}{k_{\text{diss}} \theta_{\text{CO}}}} \quad 3.10a$$

$$\frac{\theta_{\text{CO}}}{1 - \theta_{\text{CO}}} = K_{\text{ads}}^{\text{CO}} \frac{P^{\text{CO}}}{P_0^{\text{CO}}} \frac{1}{1 + \frac{k_{\text{diss}} \theta_{\text{CO}}}{k_{\text{H}}} + \frac{k_{\text{diss}} (1 - \theta_{\text{CO}})}{k_{\text{des}}^{\text{CO}}}} \quad 3.10\text{b}$$

An analytical solution is not possible because of the higher-order equation for θ_{CO} .

However, the kinetic expressions for R_{CH_4} that correspond to the two different cases can be determined analytically:

$$R_{\text{CH}_4} = k_{\text{H}}(1 - \theta_{\text{CO}}), \quad k_{\text{diss}} \theta_{\text{CO}} \gg k_{\text{H}} \quad 3.11\text{a}$$

$$\theta_{\text{CO}} \approx \frac{K_{\text{ads}}^{\text{CO}} \frac{P^{\text{CO}}}{P_0^{\text{CO}}}}{1 + \frac{K_{\text{diss}} \theta_{\text{CO}}}{k_{\text{H}}}} \ll 1, \quad k_{\text{diss}} \theta_{\text{CO}} \gg k_{\text{H}} \quad 3.11\text{b}$$

$$R_{\text{CH}_4} = k_{\text{diss}} \theta_{\text{CO}}(1 - \theta_{\text{CO}}), \quad k_{\text{diss}} \theta_{\text{CO}} \ll k_{\text{H}} \quad 3.12\text{a}$$

$$\theta_{\text{CO}} = \frac{K_{\text{ads}}^{\text{CO}} \frac{P^{\text{CO}}}{P_0^{\text{CO}}}}{1 + K_{\text{ads}}^{\text{CO}} \frac{P^{\text{CO}}}{P_0^{\text{CO}}}}, \quad k_{\text{diss}} \theta_{\text{CO}} \ll k_{\text{H}}; k_{\text{diss}} \theta_{\text{CO}} \ll k_{\text{des}}^{\text{CO}} \quad 3.12\text{b}$$

$$R_{\text{CH}_4} = k_{\text{diss}} \frac{K_{\text{ads}}^{\text{CO}} \frac{P^{\text{CO}}}{P_0^{\text{CO}}}}{\left(1 + K_{\text{ads}}^{\text{CO}} \frac{P^{\text{CO}}}{P_0^{\text{CO}}}\right)^2} \quad 3.12\text{c}$$

These equations will be analyzed in the subsection that follows.

3.3.1.2.2 The Apparent Activation Energy

In the case described by Eqs. (3.11), the apparent activation energy of the reaction is determined by the rate of surface carbon hydrogenation and the surface is mainly covered with “C” species. In the case described by Eqs. (3.12), the apparent activation energies depend on the CO coverage, which can vary.

The apparent activation energy E_{app} of the rate of methane formation now depends strongly on the coverage of CO:

$$E_{\text{app}} = E_{\text{diss}} + (1 - 2\theta_{\text{CO}})E_{\text{ads}}^{\text{CO}} \quad 3.13$$

In Eq. (3.13), E_{diss} is the activation energy of CO dissociation and $E_{\text{ads}}^{\text{CO}}$ is the adsorption energy of CO. At low CO coverage E_{app} is lower than E_{diss} because $E_{\text{ads}}^{\text{CO}}$ is subtracted. As can be seen in equation (3.12c), the order of reaction is first order in partial CO pressure. At

high CO coverage E_{app} is higher than E_{diss} , because E_{ads}^{CO} must be added to E_{diss} . The order of reaction becomes negative order in the partial pressure of CO.

There is a clear physical interpretation of these different behaviors as shown by the rate of product formation as a function of partial pressure of CO. It is typical for heterogeneous catalytic reactions ([Figure 3.9](#)).

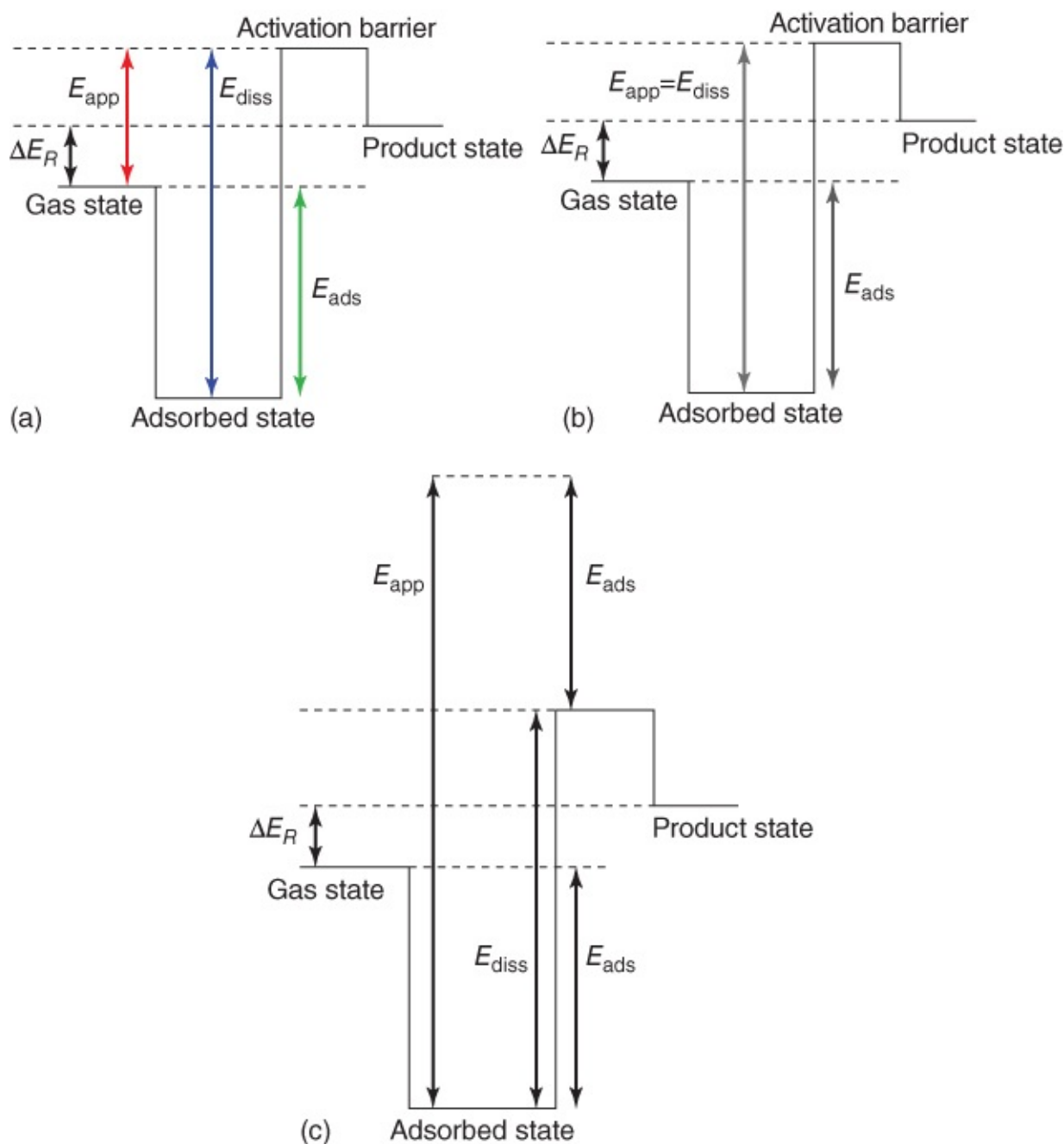


Figure 3.9 (a) $\theta_{CO} \ll 1$ and $E_{app} = E_{diss} + E_{ads}^{CO}$. (b) $\theta = 1/2$ and $E_{app} = E_{diss}$. (c) $\theta_{CO} \gg 1$ and $E_{app} = E_{diss} + E_{ads}^{CO}$. Schematic reaction energy diagram corresponding to elementary kinetics of methane formation from CO. The rate constant of CO dissociation is assumed to be rate-controlling ($E_{diss} > 0$; $E_{ads} < 0$).

In the case where θ_{CO} is substantially less than 1, the apparent activation energy is E_{diss}

measured with respect to the gas phase. When $\theta_{\text{CO}} = 1/2$, the apparent activation energy is equal to E_{diss} measured with respect to its adsorbed state. And when θ_{CO} is nearly 1, the apparent is E_{diss} to which $|E_{\text{ads}}^{\text{CO}}|$ is added. In the third case, a CO molecule must desorb in order to create a surface vacancy for the adsorption of the additional adatom generated upon CO dissociation.

As a second example, in alkene hydrogenation, when the hydrocarbon surface coverage is low the adsorption energy of the alkene must be subtracted from the activation energy of the molecule. In contrast at high coverage the apparent activation energy is equal to the molecular activation energy.

This subsection has illustrated the close relationship between surface coverage, order of reaction, and apparent activation energy for the kinetics of a heterogeneous catalytic reaction.

3.3.1.2.3 Michaelis–Menten Kinetics

We will conclude this section by showing the similarity between the kinetics of enzyme catalysis, or homogeneous catalysis by organometallic complex catalysts, and the kinetics of heterogeneous catalysis.

The reason for this equivalence is that in both types of catalysis the number of catalytic sites is a constant, and in both cases the analog of the surface coverage is the number of occupied molecular catalytic complexes. The reaction rate expression used in enzyme catalysis assumes monomolecular reaction and is called the **Michaelis–Menten equation**.

This comparison is most easily demonstrated by considering the lumped kinetics expression of heterogeneous catalytic hydrogenation of an olefin, considered as a mono molecular reaction and to compare this with the analog expression for a mono molecular reaction when catalyzed by a molecular complex or enzyme.

The Michaelis–Menten type expression for the rate of reaction is deduced if one assumes rapid equilibration between the catalyst center and free reagent and that the reaction rate is limited by the hydrogenation reaction step. In the case of hydrogenation, this would be the reaction of adsorbed hydrogen atoms with adsorbed olefin.

The lumped kinetic equation according to heterogeneous catalysis is (again we ignore explicit dependence on hydrogen pressure and concentration):

$$R_s = N_s k_r \theta \quad 3.14a$$

$$\theta = \frac{K_{\text{ads}} \frac{P}{P_0}}{1 + K_{\text{ads}} \frac{P}{P_0}} \quad 3.14b$$

The equivalent Michaelis–Menten expression in the notation conventionally used in enzyme catalysis is:

$$R_e = k_2 E_0 \frac{S}{K_m + S} \quad 3.14c$$

The overall catalytic rate is proportional to the maximum number of available sites: N_s (Eq. (3.14a)) or enzyme molecules E_0 (Eq. (3.14c)). The Michaelis constant K_m is the equivalent of $1/K_{ads}$ and the partial pressure is the equivalent of the substrate concentration S . k_r is the lumped elementary rate constant of the rate-controlling surface reaction, and k_2 is the symbol corresponding to the enzyme-catalyzed reaction.

Both expressions show that at high reactant concentration, the rate of reaction becomes a constant, independent of reactant concentration. This is due to site saturation by adsorption, represented by the term in the denominator of expression (3.14b) or (3.14c).

These expressions do not allow us to predict N_s in the surface reaction for the activation energies or orders of reaction. This is a very important issue in heterogeneous catalysis because the distribution and reactivity of reactive surface centers is not uniform, and as a result the Langmuir assumption is no longer valid.

Spectroscopically, it is still a great challenge to determine the number of active sites on a working catalyst, which is often low compared to the total number of surface atoms. In Section 3.4, we will discuss the transient kinetics approach that can be used to derive this information.

It is important to realize that the kinetic equations represented thus far do not account for the reverse reaction of the product where readsorption and reaction back to reactant leads to equilibrium between the reactant and product at long contact times of gas or liquid flow.

3.3.1.2.4 Fundamental Catalytic Kinetics Equation

Generally, the overall rate of a catalytic reaction is determined by the elementary reaction rate constants, the surface coverage of reaction sites, and a chemical driving force that is expressed as affinity A_{ff} .

The chemical affinity of the reaction is zero when reaction is at equilibrium.

For the simple case of reactant A and product B, A_{ff} is defined as:

$$A_{ff} = R_g T \ln \left(\frac{R_f [A]}{R_b [B]} \right); \quad K_{eq} = \frac{R_f}{R_b} \quad 3.15$$

R_f and R_b are the respective forward and backward rates of reactant conversion, respectively. $[A]$ and $[B]$ are the respective concentrations in the reaction mixture. R_g is the gas constant.

For a two-component system, assuming a reactant activation to be rate controlling, the rate expression that includes the back reaction becomes:

$$R = \frac{k_a K_{\text{ads}}^A [A] - k_b K_{\text{ads}}^B [B]}{1 + K_{\text{ads}}^A [A] + K_{\text{ads}}^B [B]} \quad 3.16$$

In Eq. (3.16), K_{ads}^A and K_{ads}^B are the respective adsorption constants of reagent and product. k_a and k_b are the elementary reaction rate constants due to the surface reactions of adsorbed A and B. We have normalized the rate per surface site. As in Eqs. (3.14), we assume rapid equilibration between the surface and the reactant and product phase.

Equation (3.16) can be rewritten so that it explicitly shows that the rate R is zero when reactant and product are at equilibrium:

$$R = \frac{k_a K_{\text{ads}}^A [A] \left(1 - \exp \left(-\frac{A_{\text{ff}}}{R_g T} \right) \right)}{1 + K_{\text{ads}}^A [A] + K_{\text{ads}}^B [B]} \quad 3.17$$

This leads to the Langmuir–Hinshelwood–Hougen–Watson (LHHW) expression:

$$R = k_a \theta_A \left(1 - \exp \left(-\frac{A_{\text{ff}}}{R_g T} \right) \right) \quad 3.18$$

with:

$$\theta_A = \frac{K_{\text{ads}}^A [A]}{1 + K_{\text{ads}}^A [A] + K_{\text{ads}}^B [B]} \quad 3.19$$

Equation (3.18) illustrates the three contributions to the overall rate of a catalytic reaction. These are the elementary reaction rate constant of the rate-controlling step (k_a), the fraction of the surface covered by the adsorbed species to be converted (θ_A), and the driving force of the reaction that is determined by the affinity. The expression can be readily extended to represent a case with many components. The essential assumptions are that a rate-controlling step exists and that all other reaction steps are equilibrated. In the section dealing with the simulation of the Sabatier volcano curve, we will see that at the maximum of the volcano curve this condition breaks down and a different approach must be followed.

3.3.1.2.5 Eley–Rideal versus Langmuir–Hinshelwood Kinetics

The rate expressions shown in Eqs. (3.14) and (3.18) assume that the adsorption equilibrium of the reactant and product molecules is rapidly established and that the reaction proceeds by a slow elementary reaction step in which the adsorbed molecular complex is activated by the surface.

The initial adsorption of reactants is not always necessary for the reaction. Sometimes, there is a direct reaction between gas phase molecules and adsorbed molecules. When a molecule

reacts directly with a preadsorbed molecule or surface adatom without an adsorption step, the reaction is occurring through an Eley–Rideal mechanism. Examples of this type of reaction are seen in the activation of alkane molecules by surface oxygen atoms.

3.3.2 Sabatier Principle and Volcano Curves: Brønsted–Evans–Polanyi Relations

Computational catalysis has devised methods to determine the reactivity performance indicators of a catalyst at its optimum performance. In the Sabatier volcano optimum of catalytic reaction rate plotted against surface reactivity, the rates of competing elementary reaction steps balance. There is no rate-controlling step. Kinetic expressions such as Eqs. (3.9a)–(3.9c) now must be solved without assuming one rate-controlling reaction step.

In order to construct the Sabatier volcano curve, one needs to know how the reaction rate constants of the elementary reaction rates that constitute the catalytic reaction cycle depend on surface reactivity indicators. We will discuss this in the following subsection. The Brønsted–Evans–Polanyi (BEP) relation is very useful for evaluating trends in elementary reaction rate constants as a function of catalyst composition. The BEP relation correlates the activation energies of elementary reactions with equilibrium properties such as the corresponding reaction energies. Since equilibrium properties (such as adsorption energy, which is a kinetic property) are used to calculate a reaction rate, the relationship between the rate constant and equilibrium properties and the adsorption energies can only be estimated. While no rigorous statistical mechanical theory can be used to determine this relationship, useful approximation theories have been developed for a limited class of materials and reactions.

These theories involve the use of linear activation energy–reaction energy relations between the activation energy and adsorption energies of reaction products or reaction reagents. We will explain the concept of BEP as it applies to elementary surface reaction steps in [Section 3.3.2.1](#). In [Section 3.3.2.2](#), its use will be illustrated by a simulation of the Sabatier optimum using the kinetics model of the CO to methane reaction of Eqs. (3.10).

In [Section 3.3.2.3](#), we will return to a discussion of the full catalytic reaction cycle. The concept of a reaction energy diagram and its relationship to the overall reaction rate will be introduced. The kinetics definition of the Sabatier reaction rate optimum will be given.

3.3.2.1 Brønsted–Evans–Polanyi Relations of Elementary Surface Reaction Rate Constants

The Brønsted–Evans equation relates the change in activation energy of an elementary reaction step with the change in reaction energies when the composition of a catalyst surface changes, but the structure of the reaction site remains unaltered. An example of the BEP relationship is shown in [Figure 3.10](#).

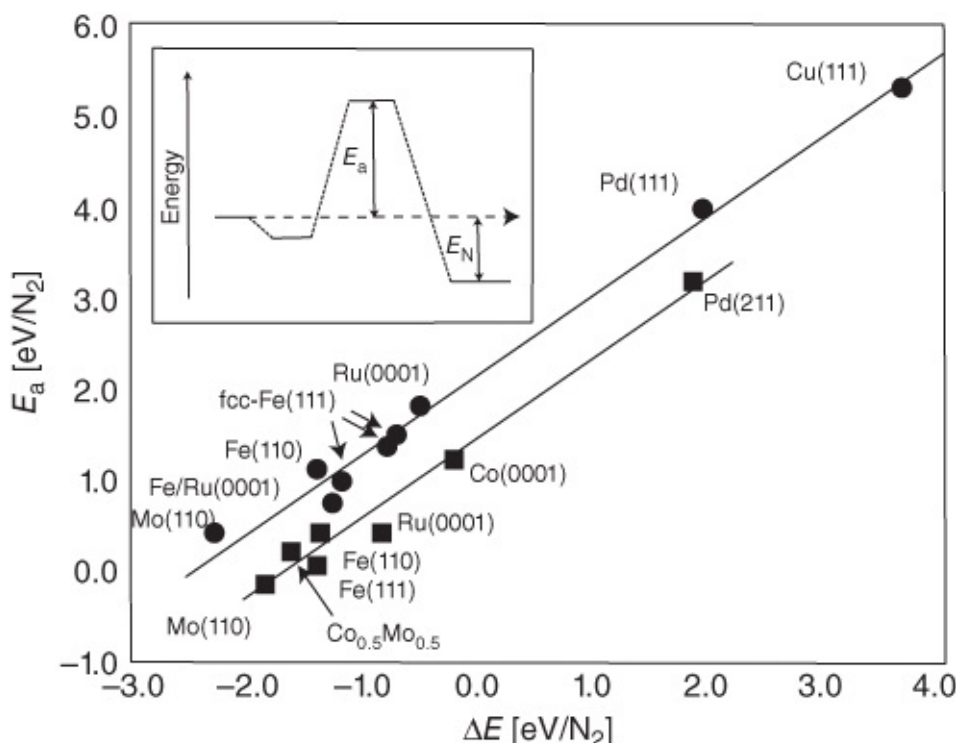


Figure 3.10 The calculated activation energies (transition state potential energies) for N_2 dissociation (E_a) on a range of metal surfaces plotted as a function of the adsorption energy for two nitrogen atoms (E_N^*). All energies are relative to N_2 (g). Results for both closely packed surfaces (filled circles) and more open surfaces (filled squares) are shown. The crystallographic orientations of the different surfaces are indicated within brackets. The inset shows a sketch of the energies for the N_2 dissociation reaction. (Dahl *et al.* 2001 [21]. Reproduced with permission of Elsevier.)

In this figure, the DFT-calculated barriers for N_2 dissociation (measured with respect to the gas phase) for two surfaces of different topologies are plotted for a variety of transition metals as a function of the adsorption energy of the N atoms. A linear dependence is observed when dissociation is compared on surfaces with the same structure. The notation of the crystallographic orientations of the different surfaces can be different when the bulk structure is varied, while the surface topology can still be similar [22].

The BEP relation applies as long as the elementary reactions are studied at reaction centers of the same structure and the reaction path of the elementary reaction steps is similar.

The BEP equations can be written as:

$$E_f^\# = E_{f,0}^\# + \alpha_b \Delta E_r \quad 3.20a$$

α_b is the BEP proportionality constant. $E_f^\#$ and $E_{f,0}^\#$ are the activation energies on two surfaces with different reactivity. ΔE_r is the change in reaction energy. When Eq. (3.20a) represents the activation energy change for the forward reaction, the equation for the activation energy of the reverse reaction is:

$$E_r^\# = E_{r,0}^\# - (1 - \alpha_b)\Delta E_r$$

3.20b

$E_r^\#$ and $E_{r,0}^\#$ are the respective values of the activation energies of the reverse reaction. The changes in activation energies are illustrated by [Figure 3.11](#).

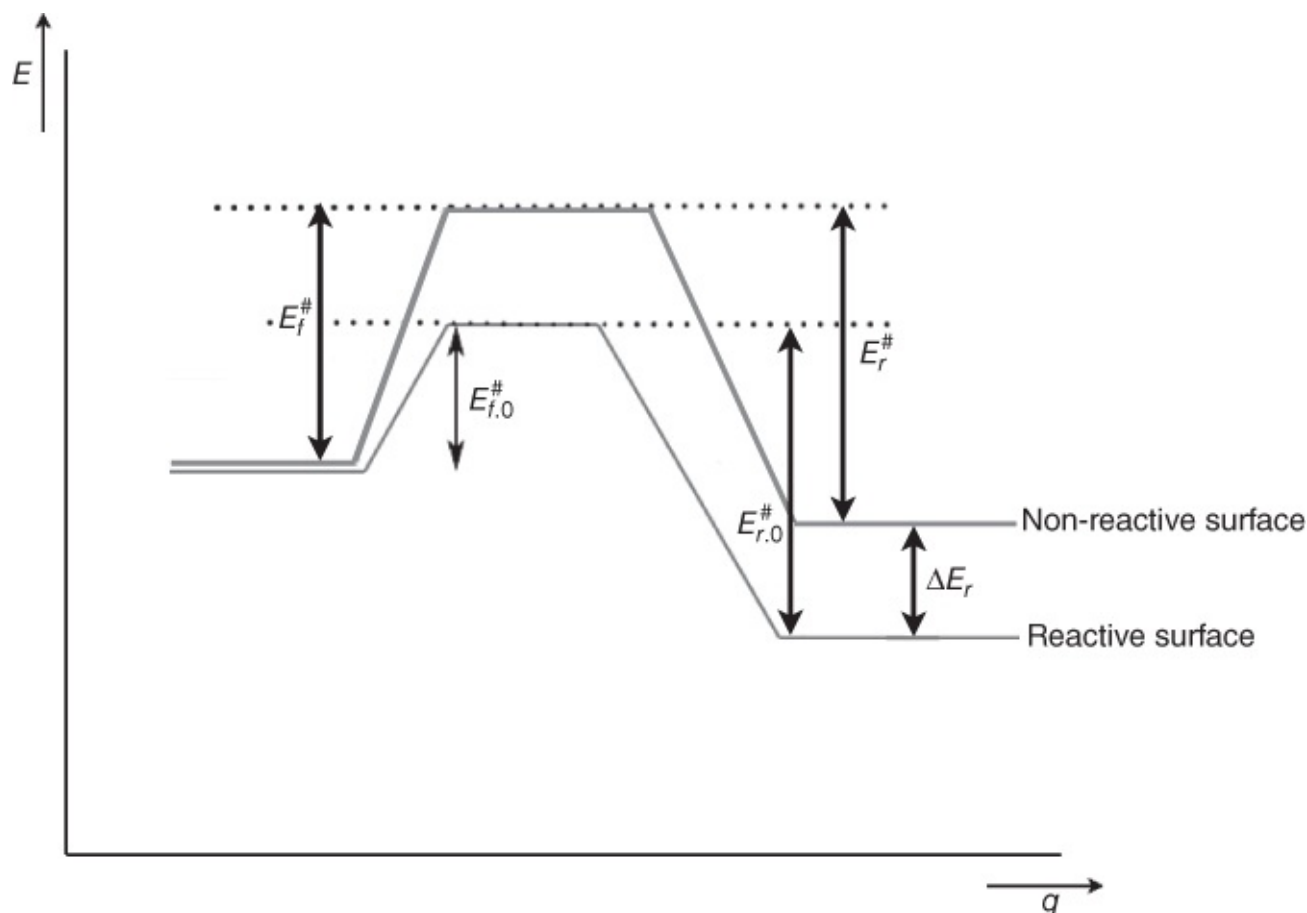


Figure 3.11 Sketch of activation energies and reaction energy according to Eqs. (3.20a) and (3.20b). Symbols are explained in the text.

The proportionality constant of forward and reverse reaction are related due to microscopic reversibility; the sum of the changes in the rate constants for the forward and reverse reactions must be equal to the change in reaction energies.

As [Figure 3.11](#) illustrates, the value of α_b is close to 1 for a dissociation reaction. As a consequence, the proportionality for the reverse association reaction of two N atoms is nearly zero. This shows that surface reactions in which adsorbate chemical bonds are broken are sensitive to a change in surface reactivity. Conversely, the activation energy of a recombination reaction is independent of surface reactivity.

The BEP relation is an example of the Brønsted relation that is widely used to correlate activation energy changes of chemically related elementary reactions with a physical parameter that changes with reaction energy [23]. For the case of the surface reactions, it is the linear relation between activation energy change ΔE_{act} and reaction energy change ΔE_r :

$$\Delta E_{\text{act}} = \alpha_b \cdot \Delta E_r, \quad 0 < \alpha_b < 1$$

3.20c

In gas phase kinetics, often a value of $\frac{1}{2}$ is chosen for α_b . The value of α close to 1 for surface dissociation reactions implies that the structures of the transition state complex and that of the final dissociated state are close. This is because to activate a chemical bond the adsorbate–surface interaction has to be so strong that in the transition state the cleaving adsorbate can be considered to be nearly broken.

Knowing the α_b values, one can predict the activation energy of an elementary reaction step for a new system once the adsorption energies of the dissociation fragments are known for one system. The structure of the reaction center must be identical to that of another metal with known activation energy and fragment energies. The advantage of this procedure is that it eliminates the elaborate process of calculating the activation energy for each new system.

Note that in [Figure 3.10](#) the least reactive transition metals are located to the right of the center in the periodic system, while metals of highest reactivity are in the center. This is caused by the nature of the bond between surface chemical and transition metal surface, which we will discuss in [Chapter 8](#).

The strong dependence of the activation energy of dissociation on changes in surface reactivity as measured by the adsorption energies of the corresponding adatoms is due to the strong interaction that is needed between surface atoms and dissociating molecular chemical bond to achieve dissociation.

The high value of α_b implies that the changes in chemical bonding interaction in the transition state complex are very similar to changes in bonding interactions for the adatoms resulting from dissociation. An important result of this strong interaction is that the molecule in the transition state becomes immobile.

The activation entropy of an elementary surface reaction is small. Although there is a large change in entropy of a molecule between the gas phase and the adsorbed state, such changes are relatively small for reactions between fragments on the surface.

The higher reactivity of the more open stepped (211) surface compared to the more dense (111) surface is due to the higher reactivity of the surface metal atoms. The surface atoms on the (211) surface are more reactive than on the (111) surface because they have a lower coordination with neighbor metal atoms. When their coordinative unsaturation increases, the strength of the atomic chemical bond with a surface adatom also increases. In addition, the stepped configuration of the (211) surface has a favorable topology for low activation energy of N_2 . This will be discussed in more detail in [Chapter 4](#).

The changes in adsorption energy of an adatom when surface atom coordination varies are illustrated by the calculated adsorption energies of a C atom to different metal surfaces of Ru as shown in [Table 3.1](#). Such trends are very similar to atoms such as C, N, or O.

Table 3.1 Adsorption energy of a C atom as a function of its coordination and surface atom coordinative unsaturation as calculated by DFT on different Ru surfaces (the crystallographic orientation of the surface of the hexagonal close-packed Ru metal are indicated within brackets; see [7] for notation)

Adsorption energies with respect to C gas phase and Ru(0001) bare surface			
Surface	Site	Adsorption energy (kJ mol ⁻¹)	Number of Ru neighbors for C (and for Ru)
Ru(0001)	Top	497	1 (9)
	Bridge	631	2 (9)
	Hollow hcp	688	3 (9)
	Hollow fcc	648	3 (9)
Ru(11 $\bar{2}$ 0)	Top up	549	1 (7)
	Top down	675	3 (7) + 1 (11)
	Bridge short	666	2 (7)
	Bridge long	579	2 (7) + 2 (11)
Ru(10 $\bar{1}$ 0)	Hollow	678	2 (11) + 1 (7)
Ru(1015)	Hcp	714	2 (7) + 1 (9)

Source: van Santen and Neurock 2006 [9]. Reproduced with permission of John Wiley & Sons.

The numbers in brackets in the column that shows the number of Ru neighbors for C (and for Ru) show the number of metal atom neighbors of the metal surface atoms and the number before it shows the number of metal atoms to which the C atom is attached.

It can be seen that the adsorption energy of the C atom increases with its coordination number of surface atoms. As long as the M–C interaction is compared for atoms adsorbed to the same number of surface atoms, the interaction with surface metal atoms with lower coordination to the nearest neighbor metal surface atoms shows an increase of the adsorption energy. This inverse relation between the strength of the adatom chemical bond and the strength of interaction of the metal atom in contact with the adsorbed nearest neighbor metal atoms will be discussed in detail in [Chapter 7](#), where we will also describe its relation to the electronic structure of the surface chemical bond. A more intuitive comprehension of this relation can be obtained by understanding the consequences of bond order conservation in chemical bonding when coordination changes. This will be discussed in the next subsection since this is very useful for understanding the differences in the reactivity of surfaces as a function of their degree of coordinative unsaturation of the surface atoms.

3.3.2.1.1 Bond Order Conservation

The concept of bond order conservation is based on the idea that for a single atom, its total binding capability with the surrounding atoms is a constant. This means that when more atoms bind to a central atom, the binding power must be redistributed over more chemical bonds and, hence, the binding power for each bond decreases. The sum of the bond orders of the chemical bonds attached to a surface atom then is approximately constant.

When a chemical bond is broken, the energy of the other remaining bonds increases to maintain a constant total bond order. This provides a qualitative explanation for the increase in reactivity of a surface metal atom when coordinative unsaturation increases, and rationalizes the weakening of internal chemical bonds of molecules adsorbed to a surface compared to the internal bonds of the free molecules (see Insert 3.3).

Insert 3 Bond Order Conservation Expression

Shustorovich [24] deduced the following expressions for the bond strength Q_n of a bond to be shared with similar neighbors:

$$Q_n = \frac{1}{n} Q_0 \left(2 - \frac{1}{n} \right) \quad 3i.1$$

Q_0 is the bond strength when bonds do not have to be shared ($n = 1$).

The consequences of this expression on adsorbate strength are shown in [Figure 3i.1](#).

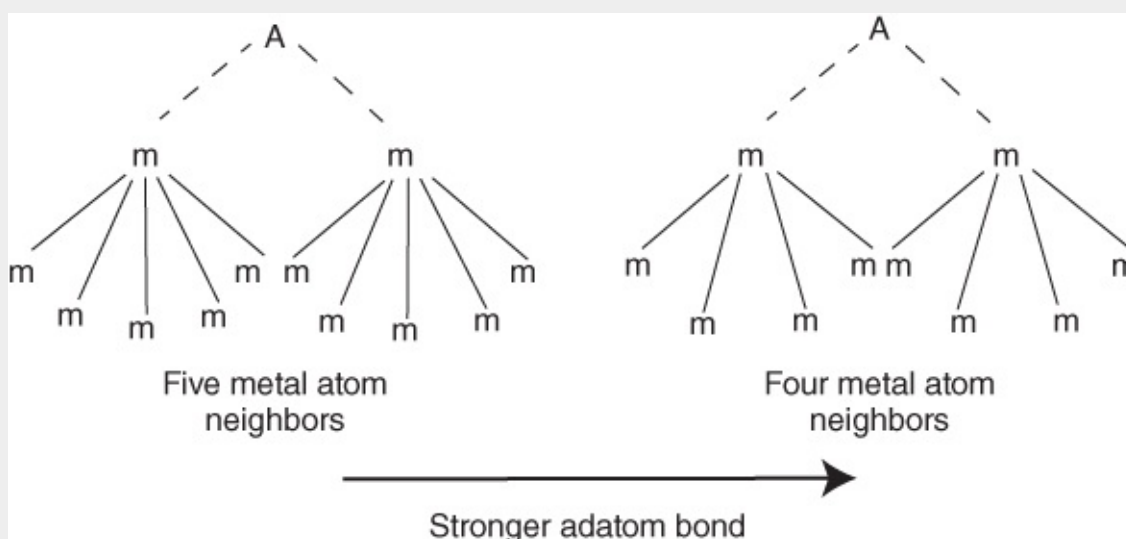


Figure 3i.1 Adatom A chemisorption as a function of metal atom coordination number m . Surfaces are more reactive when surface metal atoms have fewer neighbors.

The derivation is based on the assumption of a Morse potential between two particles ($n = 1$).

$$Q(x) = Q_0(2x - x^2) \quad 3i.2$$

$$x = e^{-\frac{r-r_0}{a}}$$

x is the bond order ($x = 1$ when the distance r between the particles is equal to equilibrium distance, and a defines the frequencies of oscillations).

Conservation of bond order implies:

$$\sum_{i=1}^n x_i = x_0 = 1 \quad 3i.3$$

3.3.2.2 The Sabatier Volcano Curve

The BEP relation can be used to deduce the optimum surface reactivity parameters that determine the maximum reaction rate. The surface reactivity is characterized by particular values of the adatom adsorption energies. The BEP approach is used to relate activation energies of elementary reaction rates with adsorption energies of the adatoms. This is done for a specific topology of the reaction site. Different reaction centers will have a different Sabatier reaction rate optimum. When this procedure is followed, a prediction can be made for the combination of surface topology and transition metal that will produce an optimum overall reaction rate.

We will illustrate this using the example of the lumped sum kinetics of the CO to methane reaction discussed in [Section 3.3.1.2](#). In this case, surface reactivity indicators are the strength of the M–C or M–O bonds.

Insert 3.4 summarizes the simulation results based on the solutions of the corresponding steady state lumped kinetic equations (Eq. (3.10)). The BEP expressions for the variation of elementary rate constants as a function of adatom adsorption energy are given in Eqs. (4i.1)–(4i.3) of Insert 3.4. For convenience of interpretation, the variation in adsorption energies of C and O have been assumed to be similar, and the CO adsorption energies are insensitive to a change in catalyst material. Parameter values have been selected for didactic purposes and do not directly refer to experimental systems. Kinetics simulations based on quantum-chemical results of physically representative catalyst models that also include differences in variations of M–C and M–O bond energies are presented in [Figure 3.13](#).

Insert 4 Simulation of Sabatier Volcano Curve Maximum

1. Brønsted–Evans–Polanyi Relations for Lumped Elementary rate Constants of the CO to CH₄ Reaction

$$k_H = k_H^0 \exp(-\beta_H^C \Delta E_{C,ads}) \quad 4i.1$$

$$k_{diss} = k_{diss}^0 \exp(\beta_d^C \Delta E_{C,ads} + \beta_d^O \Delta E_{O,ads}) \quad 4i.2$$

$$\beta = \frac{\alpha_B}{kT} \quad 4i.3$$

$\Delta E_{C,ads}$ and $\Delta E_{O,ads}$ are the differences in adsorption energy of a C adatom and O adatom, versus those on the reference surface. k_H^0 and k_{diss}^0 are the respective lumped and elementary rate constants for hydrogenation of C adatom to methane and CO dissociation on the reference surface, respectively.

β_H^C , β_d^C , and β_d^O are the BEP proportionality-related constants for the elementary

reaction steps. Because k_H and k_{diss} refer to a reaction with a chemical bond breaking step, the BEP proportionality parameters α_B will be close to 1.

2. Simulations of Volcano Curves (assume $\Delta E_0 = \Delta E_c$) Figures 4i.1–4i.3 show Sabatier volcano curves for three values of $K_{\text{ads}}^{\text{CO}}$: $K_{\text{ads}}^{\text{CO}} = 100$, $K_{\text{ads}}^{\text{CO}} = 1$, and $K_{\text{ads}}^{\text{CO}} = 0.2$, respectively. The figures compare the rate of production of methane, R_{CH_4} and surface coverages of C and CO as a function of ΔE_C . Figure 4i.4 compares simulations for different values of k_{diss}^0 with $K_{\text{ads}}^{\text{CO}} = 1$.

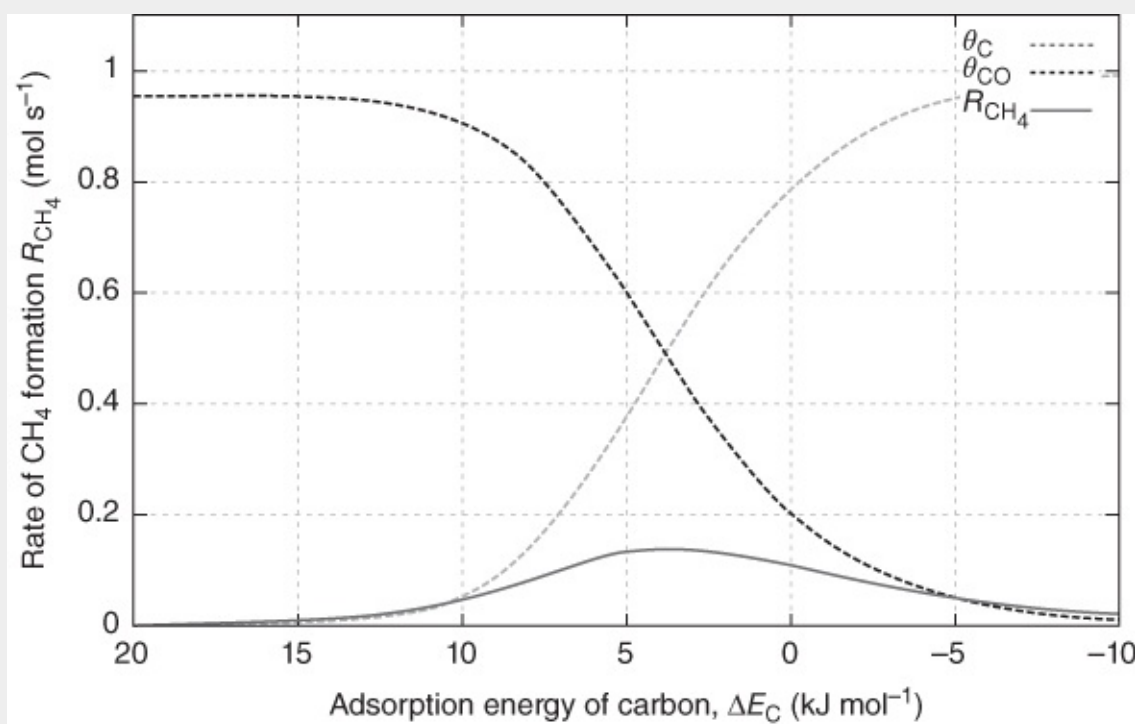


Figure 4i.1 Rate of CH_4 formation R_{CH_4} versus change in adsorption energy ΔE_c $k_H^0 = 1$, $k_{\text{diss}}^0 = 0.01$, $k_{\text{des}} = 10$, $k_{\text{ads}} = 1000$, $\beta_H^C = \beta_d^C = \beta_d^O = 1/5$.

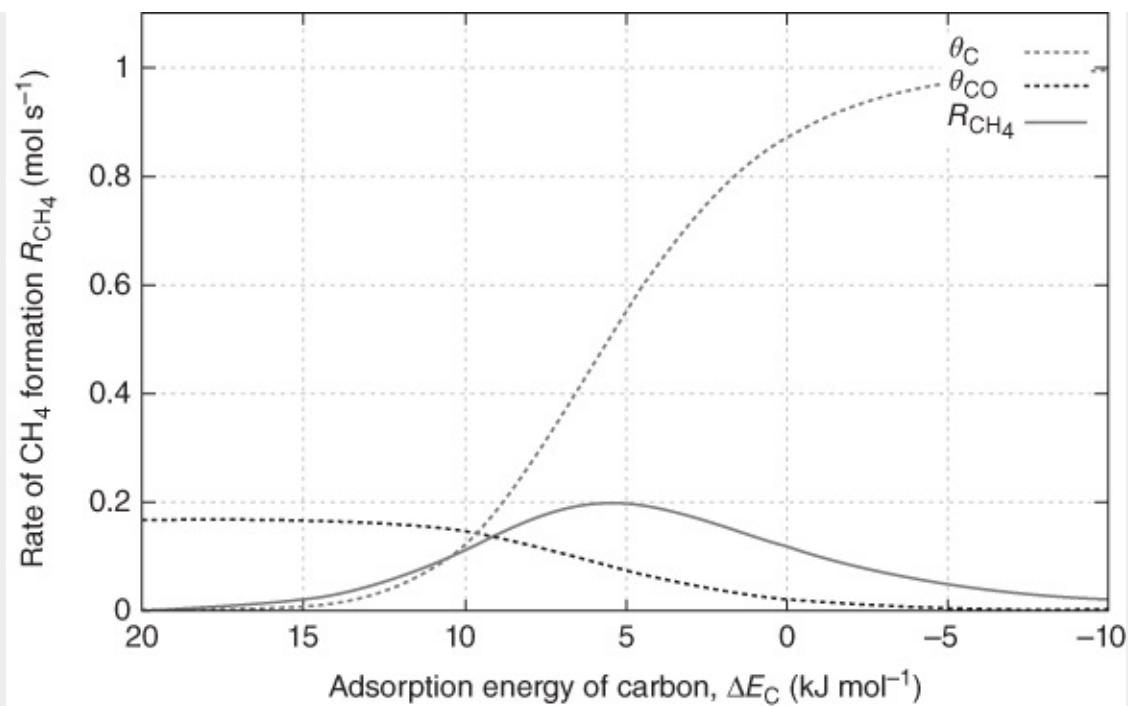


Figure 4i.2 Rate of CH_4 formation R_{CH_4} versus change in adsorption energy ΔE_c $k_H^0 = 1$, $k_{\text{diss}}^0 = 0.01$, $k_{\text{des}} = 1000$, $k_{\text{ads}} = 1000$, $\beta_H^C = \beta_d^C = \beta_d^O = 1/5$.

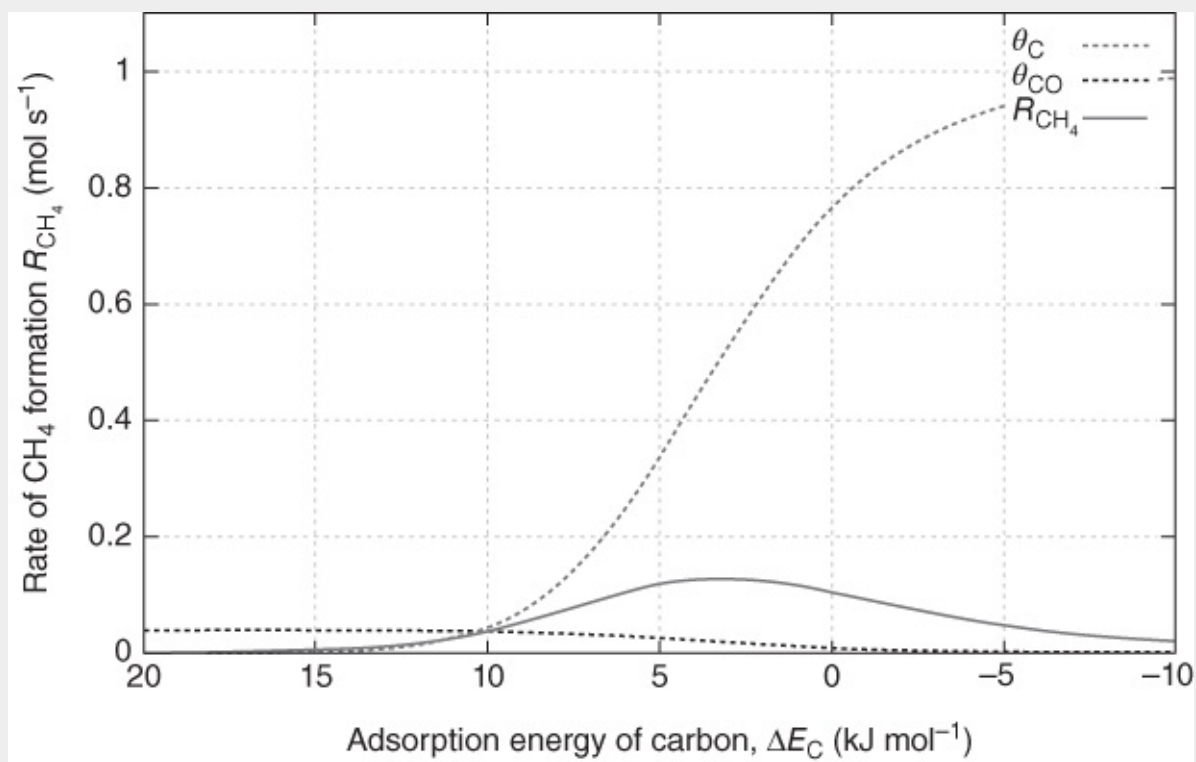


Figure 4i.3 Rate of CH_4 formation R_{CH_4} versus change in adsorption energy ΔE_c $k_H^0 = 1$, $k_{\text{diss}}^0 = 0.01$, $k_{\text{des}} = 5000$, $k_{\text{ads}} = 1000$, $\beta_H^C = \beta_d^C = \beta_d^O = 1/5$.

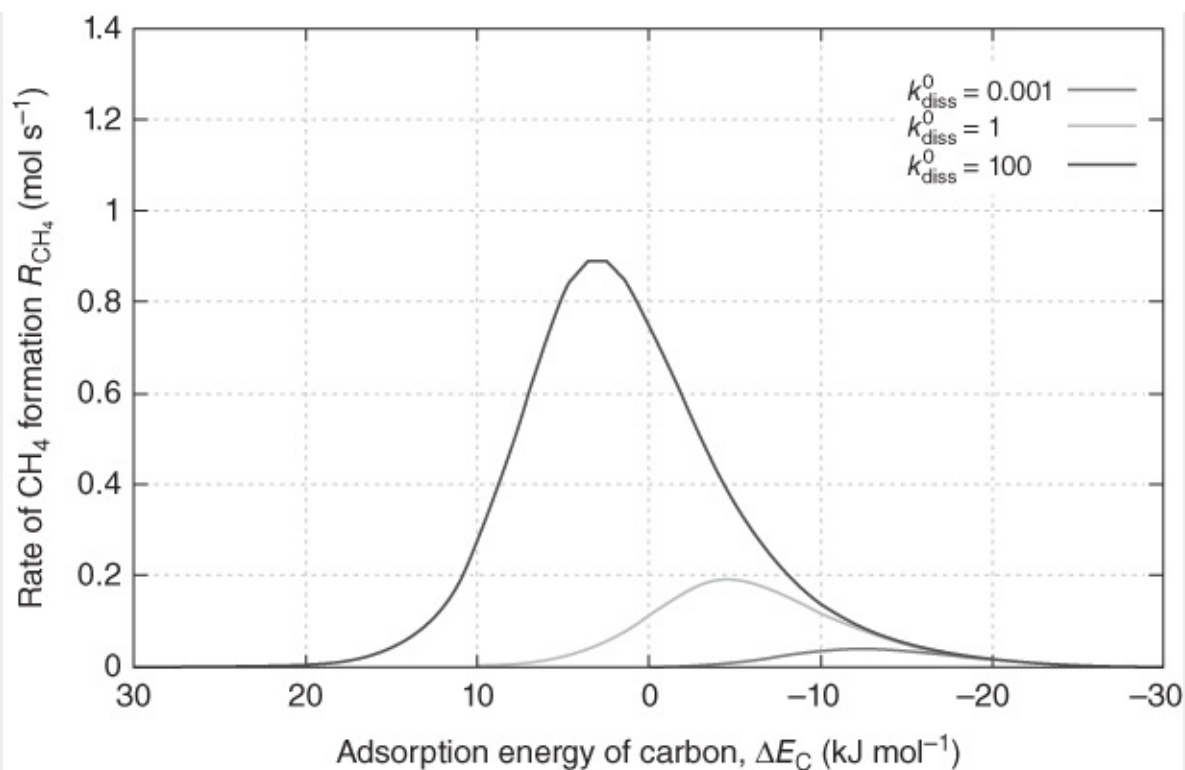


Figure 4i.4 Rate of CH₄ formation R_{CH_4} versus change in adsorption energy ΔE_c $k_H^0 = 1$, $k_{\text{des}} = 1000$, $k_{\text{ads}} = 1000$, $\beta_H^C = \beta_d^C = \beta_d^O = 1/5$.

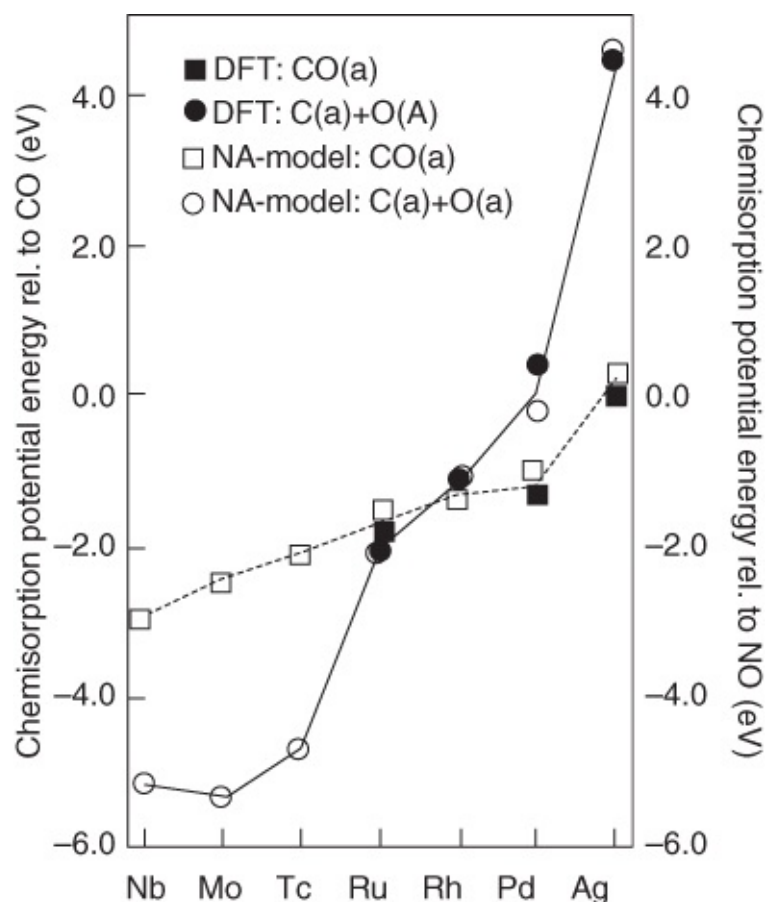


Figure 3.12 Calculated and model estimates of the variation in the adsorption energy of molecular CO compared with atomically adsorbed C and O for the most closely packed surface of the 4d-transition metals. (Hammer and Nørskov 2000 [25]. Reproduced with permission of Elsevier.)

It is reasonable to assume that the adsorption energies of CO do not vary significantly with a change in M–C bond energies. As we will explain later, this variation is minimal because the electron donative and back donative chemical bonding interactions between molecule and surface counteract and nearly cancel. This is well illustrated in [Figure 3.12](#), which compares the variation in the sum of the respective M–C and M–O adatom bond energies as computed by DFT for different metals.

As we will discuss in detail in [Chapter 7](#), the changes in the sum of adatom energies for C and O are dominated by the changes in the oxygen adatom energies; the changes in the adatom C energies are substantially less.

The simulations of Insert 3.4 assume rapid equilibration of gas phase CO with CO adsorbed to the surface. [Figures 4i.1–4i.3](#) compare simulations with different values of $K_{\text{ads}}^{\text{CO}}$, ranging from large in [Figure 4i.1](#) to small in [Figure 4i.3](#). All three figures show a maximum rate of methane production at a comparable value of E_{C} , the adsorption energy of C. This rate varies slightly with $K_{\text{ads}}^{\text{CO}}$. The surface coverages are very different in the three cases. At high CO coverage, the order in CO partial pressure will be negative, while at the low CO coverage it will become positive.

To the right of the volcano maximum, Eq. (3.11a) applies. We observe a strong increase in θ_C with increasing adsorption energy E_C . The rate of C atom removal becomes limiting and the reaction rate becomes insensitive to CO partial pressure.

The major reaction intermediates (MARI) in this case are the surface coverages that are experimentally accessible. The concept of MARI is important. It varies with change in rate controlling step and hence order of reaction.

The position of the volcano maximum is determined by the reference values k_H^0 and k_{diss}^0 as well as the ratio of the respective BEP parameters of the elementary rate constants [26]. These values will vary when surface topology alters. The sensitivity of the rate maximum with respect to the values of k_H^0 and k_{diss}^0 is illustrated by Figure 4i.4. The position of the volcano rate maximum is shifted to a lower value of the adsorption energy E_C and is substantially higher when the value of k_{diss}^0 is increased.

The rates of competing reactions balance with the Sabatier reaction rate maximum. In the reaction shown in Insert 3.4, the reaction rate constant of CO dissociation becomes comparable to the reaction rate constant of C atom removal. This implies that kinetic methods to determine the volcano cannot be based on an assumption of a rate-controlling step. The LHHW expression Eq. (3.18) that is typical in surface kinetics cannot be applied. Instead, expressions such as Eq. (3.10) that are not based on an assumption of a rate-controlling step must be used. Insert 3.5 describes a general method to solve the microkinetics ODEs without making an assumption about the rate-controlling step.

Insert 5 The Microkinetics Equations

1. The Microkinetics Equations

The initial step for constructing the ODEs is to assemble a library of elementary reaction steps and corresponding rate constants. This produces a set of $2R$ elementary reaction equations (forward and backward) and N compounds. For each unique compound, an ODE is obtained of the form:

$$\frac{d\theta_i}{dt} = \sum_j^{2R} \left(v_{j,i} k_j \prod_q^{N_i} \theta_{q,j}^{v_{q,j}} \right)$$

where θ_i is the concentration of species i on the surface, $v_{j,i}$ is the stoichiometric coefficient of compound i in reaction j , and k_j is the rate constant of reaction j .

The set of $2R$ ODEs can be solved by integrating over time until a steady state solution is reached, given by:

$$\left\{ \frac{d\theta_i}{dt} = 0 \right\}, \quad \text{for all } i.$$

The algorithm for integrating a set of ODEs over time is called an **ODE solver**.

In order to compare microkinetic simulations with experimental observations, the reaction order n_i as a function of partial pressure of reagent i , p_i , is of interest, as is the apparent activation energy $E_{\text{act}}^{\text{app}}$. These are given by Eqs. (5i.1) and (5i.2) respectively.

$$n_i = \frac{\partial \ln(r_j^+)}{\partial p_i} \quad \text{5i.1}$$

$$E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln(r_j^+)}{\partial T} \quad \text{5i.2}$$

The rate-controlling step can be determined from the rate control of a particular elementary step [27].

$$\chi_i = \left\{ \frac{\partial \ln(r_j^+)}{\partial \ln(k_i^\pm)} \right\}_{k_i \neq j, \kappa_i}, \quad \chi_i \leq 1$$

2. The Rate Constants of Adsorption and Desorption A useful expression for the rate constant of adsorption is:

$$k_{\text{ads}} = \frac{PA}{\sqrt{2\pi mk_b T}}$$

P is the pressure and A is the surface area of molecules; in the transition state, the molecule rotates freely. The corresponding expression for the rate constant of desorption is:

$$k_{\text{des}} = \frac{k_b T}{h} \frac{A(2\pi mk_b T)}{h^2} \frac{8\pi I k_b T}{\sigma h^2} \exp \left[-\frac{\Delta E_{\text{des}}}{k_b T} \right]$$

σ is the symmetry number to properly account for the number of distinguishable orientations of the molecule.

For comparison with the lumped kinetics simulations of Insert 3.4, the result of a first principle microkinetics simulation of the same reaction is shown in [Figure 3.13](#). It displays the simulated CO to methane reaction rate versus M–C and M–O adatom bond energies for a particular surface based on first principle quantum-chemical calculations and microkinetics

simulations. These microkinetics simulations are based on reaction models that explicitly contain all intermediates of the reaction. It shows a two-dimensional simulated plot of activity, or turnover frequency (TOF), which is the number of molecules converted per unit surface area and per unit time. In [Figure 3.13](#), the adsorption energy of C decreases to the right along the horizontal axis and that of O decreases moving upward along the vertical axis.

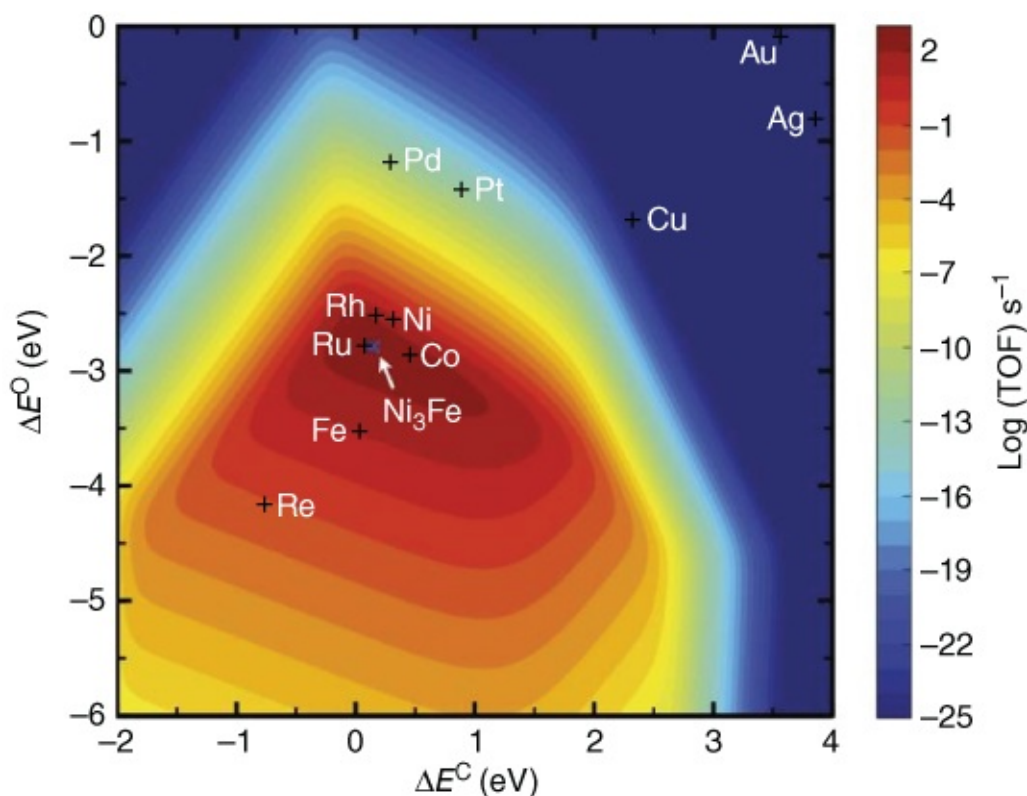


Figure 3.13 Theoretical volcano for the production of methane from syngas, CO, and H₂. The turnover frequency (TOF) is plotted as a function of carbon and oxygen binding energies. The carbon- and oxygen-binding energies for the stepped 211 surfaces of selected transition metals are depicted. Reaction conditions are 573 K, 40 bar H₂, 40 bar CO. (Nørskov *et al.* 2011 [28]. Reproduced with permission of National Academy of Sciences.)

In this figure, the contours of comparable activity are indicated. The optimum is a compromise between elementary reaction rates of CO activation, of CH_x conversion to methane, and of O atom removal by reaction with H₂.

When the adatom adsorption energy of O is too strong, the surface becomes poisoned by adsorbed O, but when the interaction is too weak, CO dissociation will be prevented by a high activation energy barrier. We find a very similar dependence on the adsorption energy of the C atoms. A surface that has the composition of Ni₃Fe appears to optimize the TOF of the reaction [28].

The determination of the Sabatier reaction rate maximum as a function of catalyst performance descriptors leads to a rational approach to improve a catalyst. By comparing the experimental results with predicted apparent activation energies and reaction orders one can determine where the experimental system is located on the Sabatier plot. This will predict in

which direction surface reactivity parameters must be changed in order to increase the reaction rate. In the above example, optimization of these parameters has been done by determining the metal combination that would give the O adatom and C adatom adsorption energies near the reaction rate maximum.

Chemical changes in surface reactivity are often realized by adding promoting compounds to the system, which alter the reactivity descriptors. Changes in surface topology can be achieved experimentally by altering the particle size of the reactive particles.

3.3.2.3 The Reaction Energy Diagram of the Catalytic Reaction Cycle

The reaction energy diagram displays the succession of energies of reaction intermediates and their respective activation energies when a reaction proceeds through its catalytic cycle. As an example, [Figure 3.14](#) shows the two reaction energy diagrams including transition state energies calculated for the reaction of CO to methane on two Ni surfaces. One of them has been used to construct [Figure 3.13](#). The reaction energy diagram shows the energy changes of all proposed reaction intermediates.

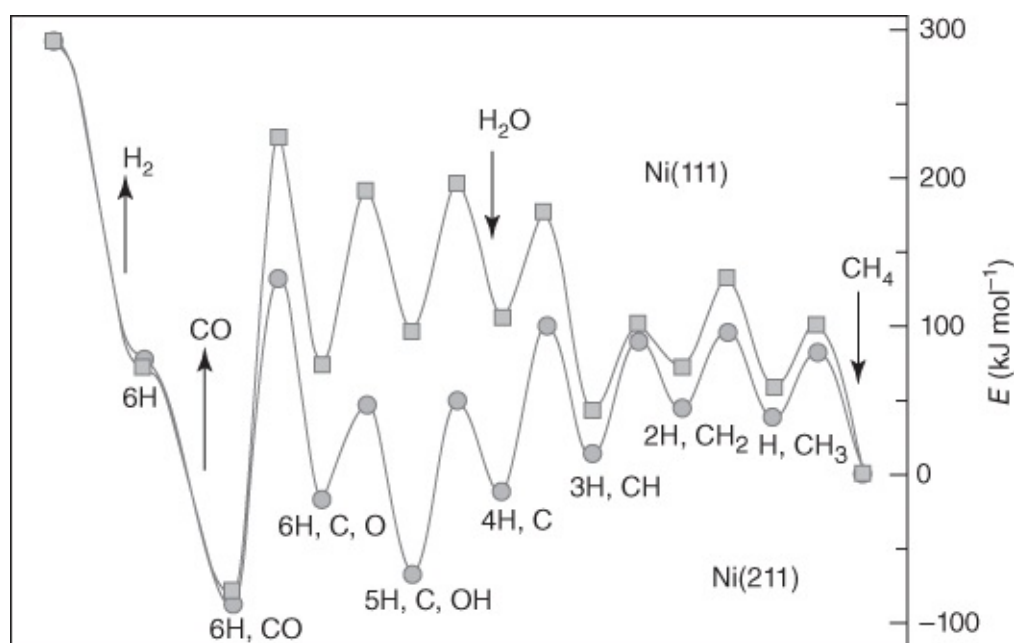


Figure 3.14 Reaction energy diagram of the methanation reaction. DFT-computed energies and activation energies are plotted with progress of reaction. Energies are given for the species adsorbed on Ni(211) and Ni(111) surfaces. The Ni(111) surface is a dense non-stepped surface, the Ni(211) surface is a more reactive stepped surface (see [7]). All energies are relative to CH_4 and H_2O in the gas phase and calculated using the results for the individual species. (Bengaard *et al.* 2002 [29]. Reproduced with permission of Elsevier.)

In order to construct a reaction energy diagram one must assume a particular reaction mechanism. In this case, it is assumed that CO adsorbs and dissociates directly. The adsorbed C and O atoms are hydrogenated in consecutive elementary reaction steps.

An alternative mechanism on Ni surfaces (which we will discuss in [Chapter 7](#), Insert 3.7) is

the initial addition of a H atom to CO and subsequent HC–O bond cleavage. H₂O can also be removed through recombination of two surface hydroxyls instead of by the direct addition of a hydrogen atom to adsorbed OH.

In [Figure 3.14](#), the energy changes are given relative to gas phase CO and H₂. The reaction products are methane and water. We observe that this reaction is slightly endothermic.

In the reaction energy diagram shown above, the energy of the system is initially lowered because the gas phase molecules CO and H₂ adsorb to the surface. H₂ dissociation has no activation barrier. The CO dissociation has a high barrier and is slightly endothermic, which raises the energy. Another local minimum is seen for adsorbed OH. From this surface state, the energy gradually increases until methane desorbs. When the reverse reaction (the steam reforming of methane) is studied, the same reaction energy diagram can be used, but the energy changes must be followed in the opposite direction.

Methane only adsorbs weakly. The initial high barrier for CH activation may indicate that CH₄ activation is a slow step. However, these reaction steps actually compete with the recombination of the adsorbed O (generated by dissociative adsorption of H₂O) and C, to give CO and the desorption energy of CO.

Reaction energy diagrams are constructed from energies calculated at 0 K and do not contain information on activation entropies, but entropy changes are sometimes essential to consider.

With respect to the gas phase, adsorbing molecules lose entropy, but desorbing molecules gain energy.

This can have important consequences for kinetics. At a finite temperature, the free energy of activation of the dissociative adsorption of CH₄ will be higher than its activation energy barrier because of the loss in entropy with respect to the gas phase, and CO desorption has a substantially lower free energy of desorption compared to its desorption energy. On the other hand, there is hardly any difference between the free energy of activation and the activation energy for the surface reaction of CO dissociation because of the low activation entropy of the surface reaction. For steam reforming this makes methane activation the rate-controlling step. Insert 3.7 (pp.97) provides an example of the simulated kinetics of these reactions as a function of temperature.

The reaction energy diagram provides insights into the condition where the heterogeneous catalytic reactions has its maximum rate. As the reaction progresses, the energy of the system goes through a minimum and the surface reaches a state where it is covered with the MARI. To recover the vacant catalyst sites, the energy must climb from its minimum in order to produce molecules that desorb at the end of the reaction cycle.

The role of the catalytically active surface is to stabilize intermediate reaction products that result from the phase of cleavage of chemical bonds. There is an energy cost to remove reaction fragments from the surface. The optimum surface condition for the maximum rate of a catalytic reaction is reached when the interaction energy with reaction intermediates is low

enough to cause desorption of the product at a low activation energy, but still high enough to activate them.

This leads to the conditions for the maximum Sabatier reaction rate based on general considerations of the reaction energy diagram, summarized in Insert 3.6. The deviations of the minimum of the reaction energy diagram below the equilibrium free energy and the maximum activation energy of the reaction above the equilibrium free energy of reaction are to be minimized with respect to the equilibrium free energy of the reaction.

Insert 6 Minimum Deviation from the Equilibrium Free Energy Requirement

An endothermic reaction can be achieved at a temperature where free energies G of the reactant and product are the same. The reaction-free energy diagrams are sketched below for three endothermic cases. For each of the three cases (a–c), the expression for overall rate R and apparent activation energy E_{app} are given. Case (d) gives the reaction energy diagram for an exothermic reaction that is not at equilibrium ([Figure 6i.1](#)).

- *Endothermic reaction*

Case (a): $|G_{\text{ads}}^{\text{B}}| > E^{\#}; \quad R = k_{\text{des}}^{\text{B}} \theta_{\text{B}}; \quad E_{\text{app}} = |E_{\text{ads}}^{\text{B}}|$

Case (b): $|G_{\text{ads}}^{\text{B}}| < E^{\#}; \quad \theta_{\text{A}} \approx 1; \quad R = k_{\text{r}}^{\text{A}}; \quad E_{\text{app}} = E^{\#}$

Case (c):
 $|G_{\text{ads}}^{\text{B}}| < E^{\#}; \quad \theta_{\text{A}} \ll 1; \quad R = k_{\text{r}}^{\text{A}} \theta_{\text{A}}; \quad \theta_{\text{A}} = K_{\text{ads}}^{\text{A}} P_{\text{A}} \ll 1; \quad E_{\text{app}} = E^{\#} - |E_{\text{ads}}^{\text{B}}| > 0$

- *Exothermic reaction*

- **Case (d):** $|E_{\text{ads}}^{\text{A}}| > E^{\#}; \quad \theta_{\text{A}} \ll 1; \quad R = k_{\text{r}}^{\text{A}} \theta_{\text{A}}; \quad E_{\text{app}} = E^{\#} - |E_{\text{ads}}^{\text{A}}| < 0.$

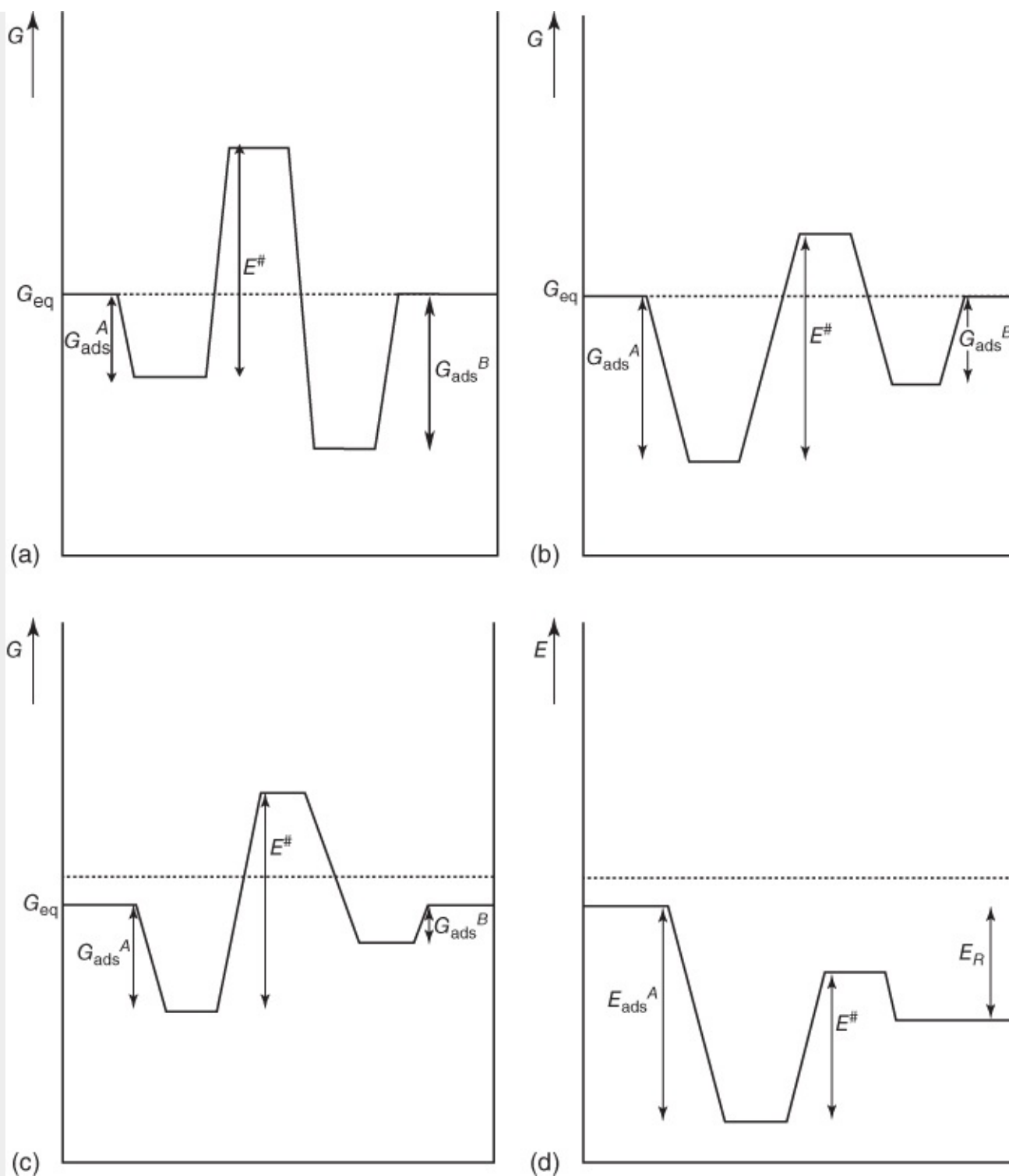


Figure 6i.1 The reaction free energy diagrams for three endothermic cases (a–c) and for an exothermic reaction that is not at equilibrium (d).

In case (a), desorption of product B is rate controlling, so that $E_{app} = E_{ads}^B$. In case (b), the rate constant k_b indicates that product desorption is fast, and the coverage of reactant A is high. The apparent activation energy becomes $E_{app} = E^\ddagger$, the activation energy of reaction with respect to the adsorbed state of A.

Case (a) is the high temperature case when $\theta_A \ll 1$, so that $E_{app} = E^\# - |E_{ads}^A|$.

The reaction rate has its maximum value when $E_{app} \approx 0$. The cases together show that deviations of activation energies in adsorption surface energies should be minimized with respect to the equilibrium free energy values of the reactant and product.

Case (d) gives an example of an exothermic reaction energy diagram. Again, when $\theta_A \approx 1$: $E_{app} = E^\#$ and when $\theta_A \ll 1$: $E_{app} = E^\# - |E_{ads}|$. Since a high level of surface coverage is beneficial to a reaction, in several catalytic systems $|E_{ads}| > E^\#$. This implies that at high temperature, the apparent activation energy may become negative.

An insightful way to appreciate the need for minimizing the difference between the free energy of the overall reaction and the free energies of intermediate adsorption or activation is provided by the energetics of the electro-catalytic oxygen evolution reaction (OER) of water by transition metal oxide electrodes, to be discussed in the next section.

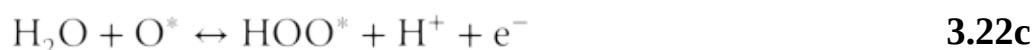
3.3.2.4 Electrocatalysis and Sabatier Principle Optimum

The overpotential of the electro-catalytic H_2O decomposition to H_2 and O_2 is mainly caused by the low rate of the O_2 evolution reaction at the anode. The half reaction that corresponds to this reaction is:



The surface reactivity descriptor in this case is the adsorption energy of the O atom, which through bond order conservation (see [Section 3.3.2.1.1](#)) can be correlated with the interaction energies of the other reaction intermediates OH and OOH.

The four reaction steps of the reaction are as follows:



An elegant thermodynamic procedure has been devised [30] that enables a quantum-chemical calculation of the reaction steps in Eqs. (3.22), with the replacement of $H^+ + e^-$ by $\frac{1}{2}H_2$.

Since the energy difference is that of the hydrogen electrode, it is the equivalent of zero electrochemical potential. The contribution to the electrode potential of the reaction can be found by the additional use of Faraday's constant to relate free energy to electrode potential:

$$\Delta\mu = Z \cdot F \cdot \Delta U$$

$\Delta\mu$ is the change in chemical potential, Z is the number of electrons transferred, F is the Faraday constant, and ΔU is the electrochemical potential contribution. When an external potential is used, the free energies of reaction change by $-Z \cdot U$. Since each of the reactions generate one proton, the differences in free energy are independent of proton concentration.

A schematic illustration of the thermodynamic reaction energy diagram one obtains for the reaction sequence of Eq. (3.22) is shown in [Figure 3.15](#).

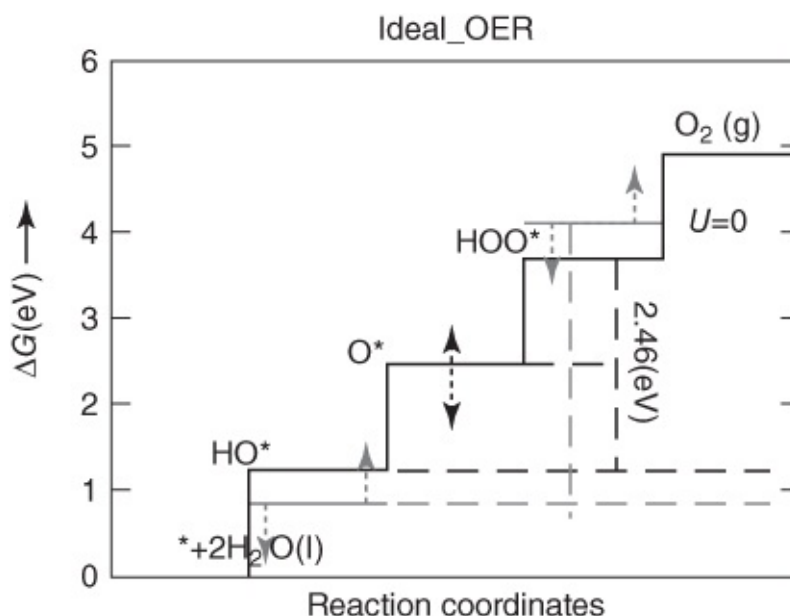


Figure 3.15 The free energy diagram for the OER ideal catalyst. All free energies of the intermediate steps have the same magnitude and are equal to 1.23 V (thick black line). Gray lines indicate the actual HOO* and HO* levels for the catalysts, which, in order to approach the ideal, must be moved down and up, respectively, by about 0.37 eV. Unfortunately, when the metal oxide catalyst is changed, these two levels tend to move in the same direction with the same magnitude (as indicated by the gray and black arrows). For the OER, the position of the O* level between the HOO* and HO* levels governs the potential determining step. (Valdés *et al.* 2012 [30]. Reproduced with permission of Elsevier.)

This figure shows an ideal curve according to the Sabatier optimum (the black curve) as well as a curve typical for a practical case (the gray curve).

In the electrocatalytic reaction, the role of the apparent activation energy is superseded by the overpotential η . When the overpotential η is zero, the electro-potential of the reaction is equal to its thermodynamics value. For the OER, the thermodynamic electro-potential is 1.23 V. In [Figure 3.15](#), the free energy of O₂ formation is plotted and corresponds to 4×1.23 eV. The overpotential of reaction is found when the potential U is shifted downward by $Z \times 1.23$ eV for each electron transferred. Z is the number of electrons transferred.

For the ideal curve shown in [Figure 3.15](#), this shifts the free energies of all intermediates on the reaction equilibrium line. In this ideal curve, the free energy changes in each reaction step are the same. As long as one ignores activation energies of the surface elementary steps, one

predicts that the electrochemical reaction does not require any additional potential to proceed because the overpotential for the ideal case is predicted to be zero. (A critical discussion on the assumptions involved can be found in [Section 11.6.2](#)). The ideal reaction energy plot in [Figure 3.15](#) therefore represents the diagram that corresponds to the Sabatier optimum of the reaction.

This ideal diagram cannot be realized in practice due to bond order conservation relations that constrain the energies of some reaction intermediates. This holds true for the bonds of OH and OOH with the catalyst surface that are chemically equivalent [31]. The energy difference that exists between the two relates to the presence of an O–OH bond in the peroxide versus an O–H bond in the hydroxyl. Therefore, changes in adsorbate M–O bond energies will affect the energies of both intermediates similarly. The difference in the free energies of those intermediates that are part of [Figure 3.15](#) can therefore never be reduced. Calculations indicate that the overpotential of this reaction can never become less than an estimated 0.4 V, which is a substantial energy loss compared to the equilibrium electrode potential of the reaction.

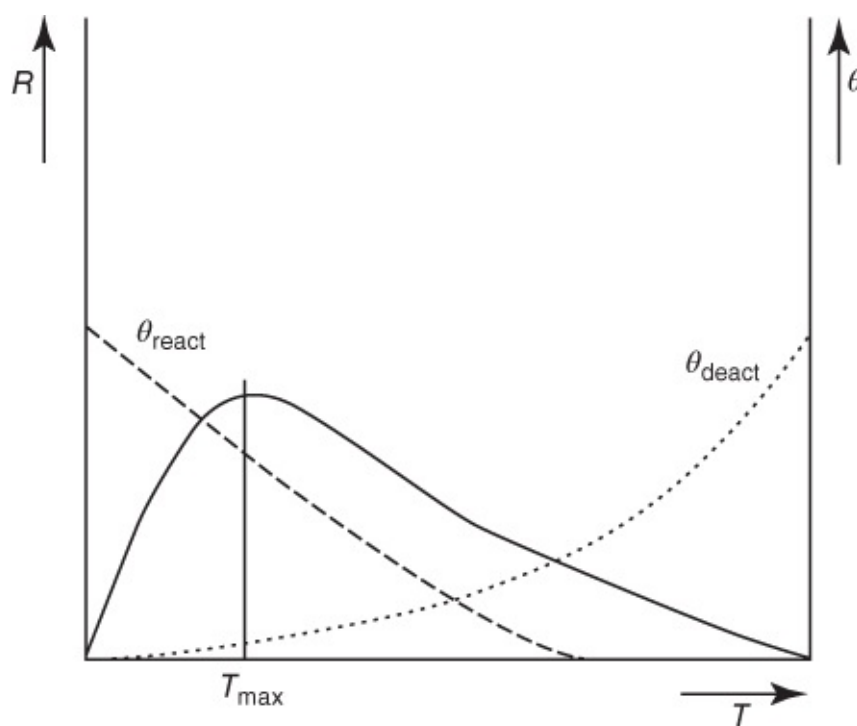


Figure 3.16 Schematic representation of the dependence of reaction rate R of a heterogeneous catalytic reaction on temperature T . The dependence of reactant surface coverage θ_{react} is also shown (dashed line). The possible increase in surface concentration of a deactivating compound θ_{deact} that is formed with higher temperature is indicated (dotted line). When no deactivating compounds are formed, there is an increase in surface vacancy concentration.

3.3.2.5 Temperature Dependence of Catalytic Reaction Rate

While the rate of a non-catalytic homogeneous reaction will increase with temperature until

equilibrium is reached, the temperature dependence of a catalytic reaction is very different. A heterogeneous catalytic reaction will always go through a maximum conversion rate as a function of reaction temperature and then decrease. This is schematically illustrated in [Figure 3.16](#).

At a low temperature the reaction cannot occur because the surface is saturated with adsorbate. The reaction will reach a finite rate only when temperature is increased to cause desorption thereby creating vacant sites to accommodate the molecular fragments generated by dissociative activation of the adsorbed molecules. Alternatively, surface vacancies are needed to adsorb co-reactant molecules.

At higher temperatures, the rate of reaction is again inhibited. Reagents will no longer adsorb to the catalyst surface for reaction, because surface coverage becomes limited by the reduced adsorption equilibrium constant. At the highest reaction temperature, the surface sites may become completely vacant or alternatively become covered by deactivating adsorbed species due to non-selective reactions (for instance, surface carbon generated as a by-product in hydrocarbon conversion reactions). Generally, the reaction order of the reaction will be negative or zero at the low temperature edge of the temperature–reaction rate (T – R) plot, but positive at the high temperature edge of the T – R plot.

In the low-temperature area of the T – R plot the apparent activation energy E_{app} is positive. It decreases gradually until it becomes zero at the T – R plot maximum and then becomes negative to the right of the T – R maximum. Case (d) of Insert 3.6 shows a reaction energy diagram that explains how the apparent activation energy can become negative. This occurs when surface coverage becomes low and the energy of adsorption is higher than the activation energy of the rate-controlling reaction.

As we have shown in Eqs. (3.11) and (3.12) and illustrated in Insert 3.6, the negative value of E_{app} beyond the rate maximum can be directly related to a decrease in surface coverage. For a highly covered surface, the apparent activation energy relates to elementary reaction activation energies with respect to the adsorbed state, but with increasing temperature the surface coverage decreases and the apparent activation energy is related to elementary reaction activation energies with respect to the gas phase.

In Insert 3.7, this behavior of rate versus temperature is illustrated by microkinetics simulations of the methanation reaction and the steam reforming reaction ([Figures 7i.1–7i.4](#)).

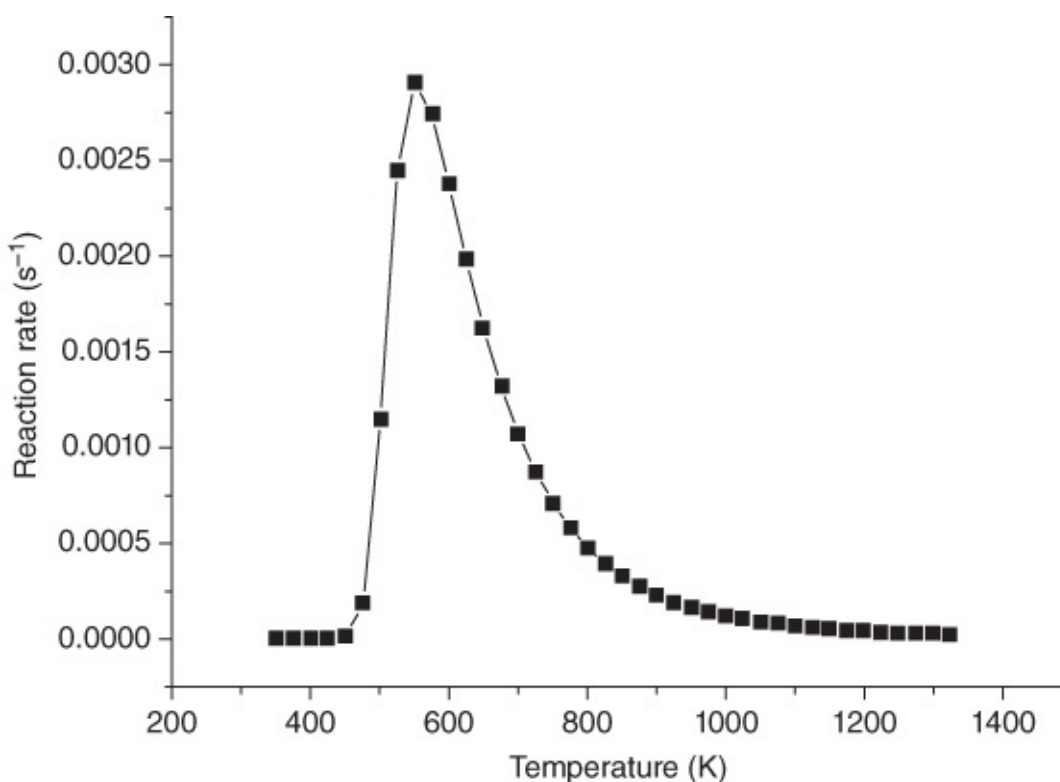


Figure 7i.1 Simulation of the production rate of methane in the methanation reaction catalyzed by Ru(0001) surface at 20 bar pressure, with a hydrogen:CO ratio of 3. The Ru(0001) surface is the dense surface of the hexagonal close-packed metals structure of Ru. (After [32, 33].)

Insert 7 The Rate of a Heterogeneous Catalytic Reaction as a Function of Temperature

Microkinetic simulations based on quantum-chemical elementary reaction rate data are presented for the methanation reaction and the steam reforming reaction (see [7] for surface structures) ([Figures 7i.5](#) and [7i.6](#)).

1.

The methanation reaction: $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$, catalyzed by the Ru(0001) surface [34]. The Ru(0001) surface is the dense surface of the hexagonal close-packed metals structure of Ru [7]. The adsorption energy of CO has been adapted to 120 kJ mol^{-1} , in order to predict the rate maximum at the proper temperature. DFT calculations tend to predict strong CO adsorption.

[Figures 7i.1](#) and [7i.2](#) show simulated temperature dependence of product formation and the corresponding surface coverages. At low temperature, the surface is covered with CO that is initially replaced by hydrogen and then by vacancies at higher temperatures.

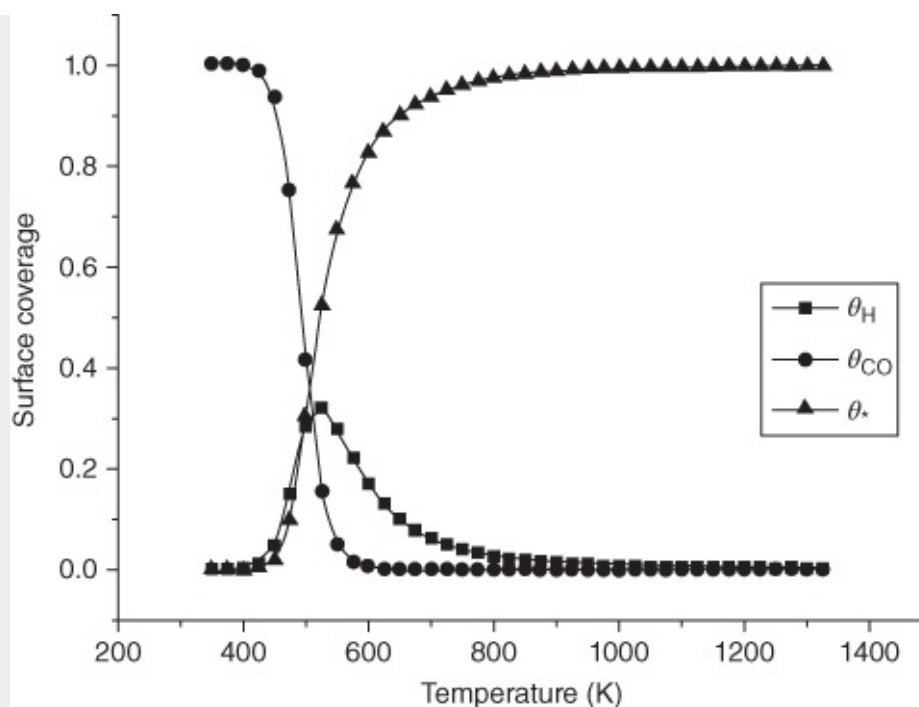


Figure 7i.2 The corresponding surface coverages of [Figure 7i.1](#) at 20 bar pressure, with a hydrogen:CO ratio of 3. (After [32, 33].)

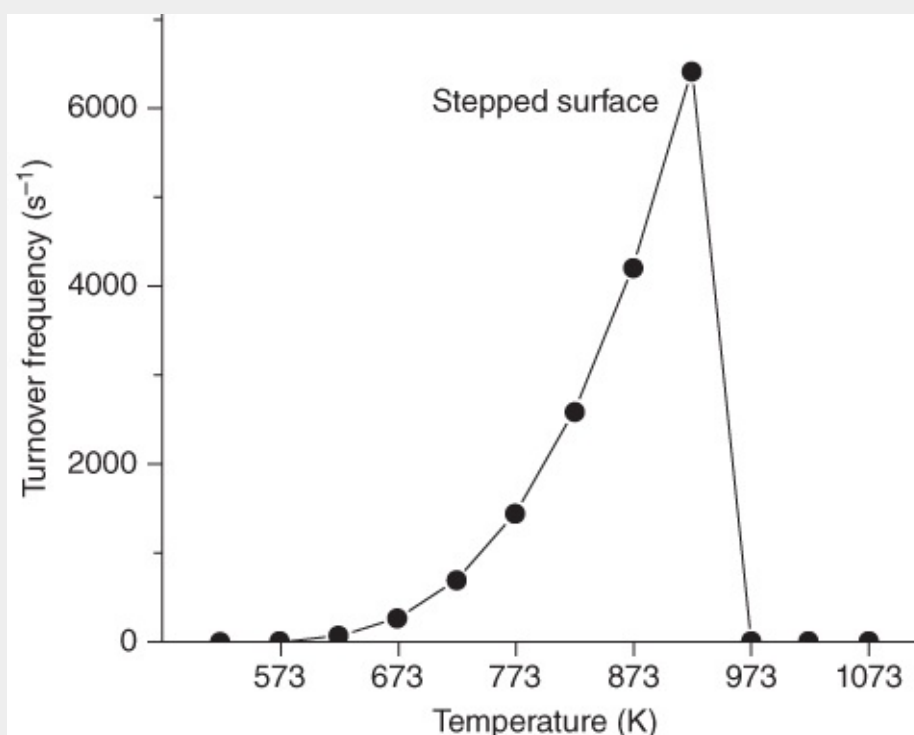


Figure 7i.3 Turnover frequency (in s⁻¹) of methane in steam methane reforming on the Rh(211) surface as a function of temperature (in K). CH₄ activation is fast, pressure is 1 bar, with CH₄:H₂O 1 : 3. (After [32, 33].)

2.

The steam reforming reaction: $H_2O + CH_4 \rightarrow CO + 3H_2$, is catalyzed by the open Rh(211) surface of the Rh face-centered cubic structure.

We compare two scenarios. In one case, the elementary reaction rate of CH_4 activation is relatively fast [33], and in the other case the elementary reaction rate of methane activation is slow.

a.

[Figures 7i.3](#) and [7i.4](#) show the results of microkinetic simulations with a relatively fast rate of methane activation.

The steep decline in reaction rate at high temperature is due to replacement of surface vacancies by deactivating C atom coverage.

b.

[Figures 7i.5](#) and [7i.6](#) show the results of microkinetic simulations with a relatively slow rate of methane activation.

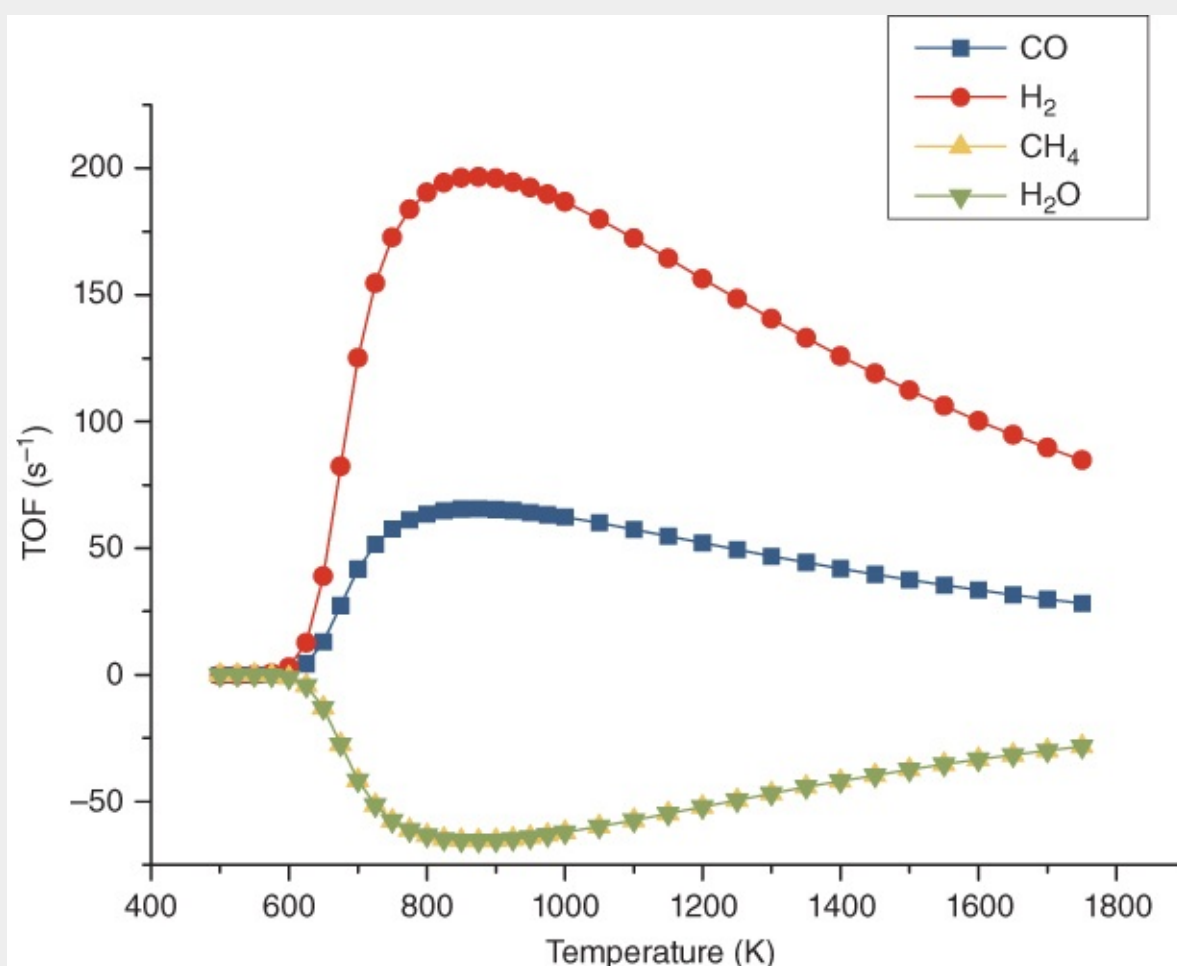


Figure 7i.5 Microkinetics simulations of the steam reforming reaction catalyzed by Ru surface assuming slow methane activation. Methane and H_2O consumption overlap. Reaction conditions are similar to those used in [Figures 7i.3](#) and [7i.4](#). (After [34].)

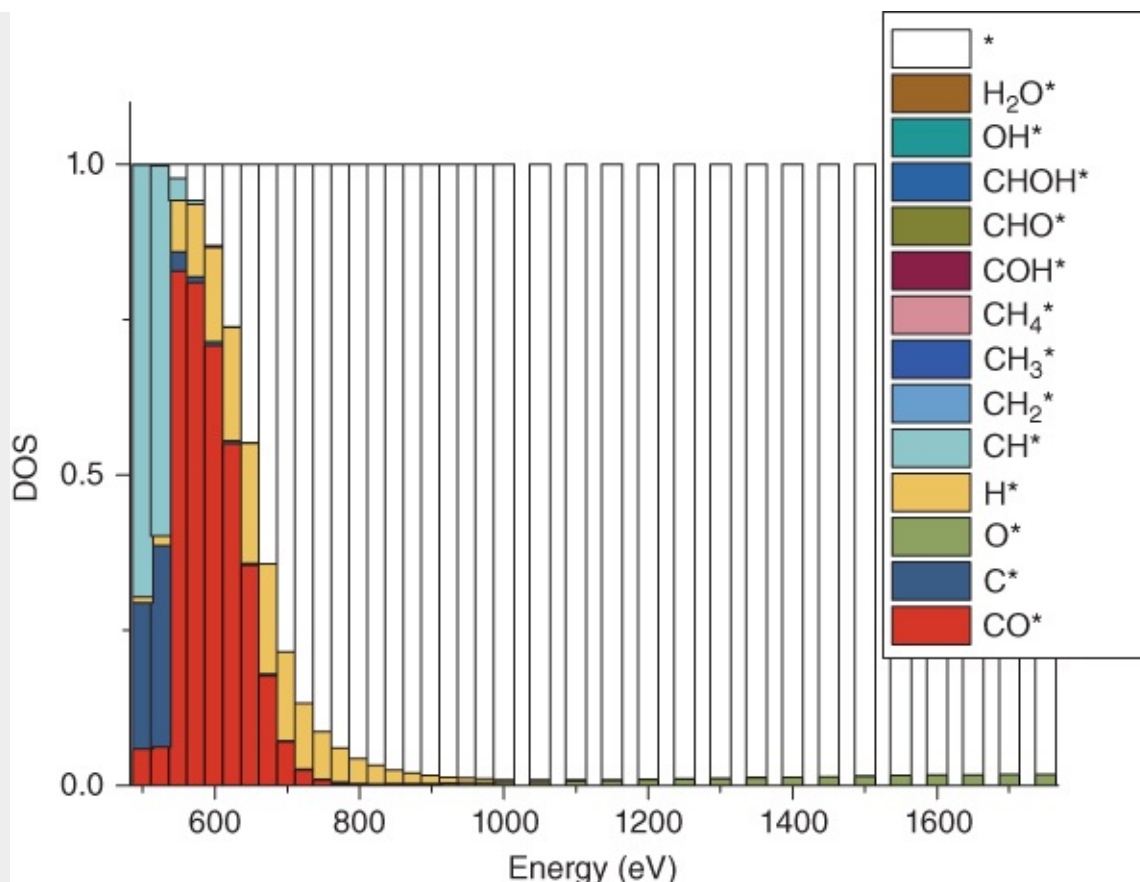


Figure 7i.6 Surface coverages as a function of temperature that correspond to the simulation results of [Figure 7i.5](#). (After [34].)

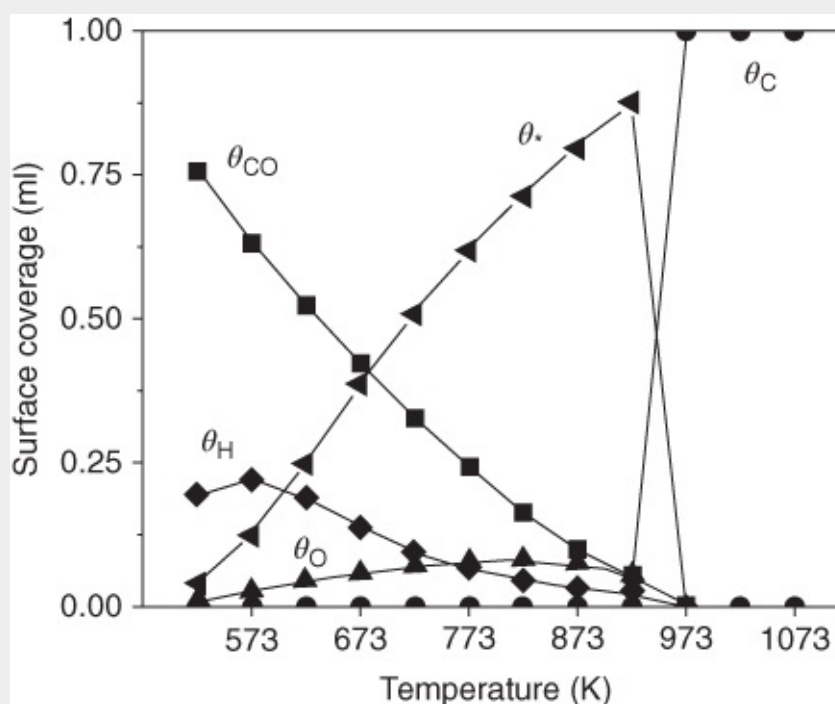


Figure 7i.4 The steady-state surface coverage (in ml) as a function of temperature (in K) corresponding to [Figure 7i.3](#). The surface coverages for the species not indicated in the graph are less than 0.01 ml. Methane activation rate is fast. (Adapted from [33].)

In the methanation reaction, CO is converted with H₂ to methane. Its lumped sum kinetics scheme has been discussed in [Section 3.3.1.2](#). The data shown in Insert 3.7 are derived from microkinetic simulations based on all elementary reaction steps.

An example of a reaction energy scheme based on a particular assumed mechanism for this reaction is shown in [Figure 3.14](#). In contrast to that mechanism, the simulations shown in Insert 3.7 also include additional steps to direct CO dissociation as C–O bond cleavage through intermediate formyl formation and H₂O formation through OH–OH recombination [32, 34].

In the figures of Insert 3.7 the changes in surface concentration of key reaction intermediates are also shown. For the CO methanation reaction, the dominant surface intermediate is CO. The rate-controlling step of the reaction is the CO dissociation reaction. The lowest barrier for C–O bond cleavage is provided by a reaction path that proceeds through the hydrogen-activated C–O bond cleavage reaction path (see [Section 7.3.2](#)). At high temperatures, the rate of reaction will decrease. The apparent activation energy of the overall reaction will become negative, since the activation energy of hydrogen-activated C–O bond activation of 110 kJ mol⁻¹ is less than the desorption energy of CO of 120 kJ mol⁻¹ (condition (d) of Insert 3.6).

In Insert 3.7, two cases are compared for the steam reforming reaction: the case where CH₄ activation is relatively fast as found for Rh, and the case where CH₄ activation is relatively slow, as found for Ru.

In the first case, the recombination reaction of CH_x and O is initially rate controlling. This reaction competes with the rate of O atom removal which has the higher activation energy. Thus, at the higher temperature surface coverage with O decreases with increasing temperature, whereas that of CH_x continues to increase. CH_x can no longer be removed from the surface, so the surface becomes covered with carbon that poisons the reaction. In the second case, the maximum reaction rate relates to the increasing coverage of the surface by CO and its subsequent desorption. Activation of methane competes with that of CO desorption.

3.3.2.6 Summary: The Order of Reaction Rate

The dependence of reaction rate on reaction mixture concentrations is often expressed by a power-law expression of the reaction rate:

$$R_{\text{PL}} = k_{\text{app}}[A]^x \cdot [B]^y \quad 3.24a$$

For the reaction of reagents A and B in Eq. (3.24a), the powers x and y determine the concentration dependence. When x and y are equal to one such an expression would represent the mass-action law rate expression of the chemical reaction.



For a catalytic reaction the reaction rate is a complex function of surface coverage, so that the

powers x and y as well as k_{app} are not true constants of the reaction rate expression. Instead, they are a strong function of reaction conditions and can only be expected to behave ideally (with a constant apparent activation energy and orders of reaction independent of condition) in a very limited temperature and pressure regime.

The change in kinetics in a Sabatier volcano curve plot as a function of surface reactivity is an example of a change in reaction orders, when the interaction of the reaction intermediates with the surface is varied. When the interaction energy is weak, the rate of reaction is positive order in the reagent, but when the interaction energy increases, the reaction order becomes zero or even negative. This change in reaction order is accompanied by an increase in the surface concentration of reaction intermediates.

The reaction rate of the catalytic reaction exhibits a maximum as a function of temperature. At low temperature, the rate of the reaction has a zero or negative order in the concentration of one of the reagents, but beyond the maximum this partial reaction order becomes positive. The surface concentration of this component changes from high to low.

Nearly all catalytic transformation reactions (except truly monomolecular reactions such as isomerization reactions) are reactions between at least two components.

For the monomolecular isomerization reaction, the rate expressions are given by Eqs. (3.14a) and (3.14b). The concentration dependence of the reaction order follows the Langmuir expression of Eq. (3.14b) as shown in Figure 3.5. With increasing concentration, the reaction order decreases from 1 to 0 and the surface concentration saturates. Insert 3.5, Case (d) provides an analysis of the change in concentration of the reagent.

For non-monomolecular reactions, the reaction rate will always show a maximum as a function of pressure of reagents due to competitive adsorption of reagents. This is illustrated in Figure 3.17 for the case where the adsorption of one of the reaction components is stronger than the adsorption of the other component.

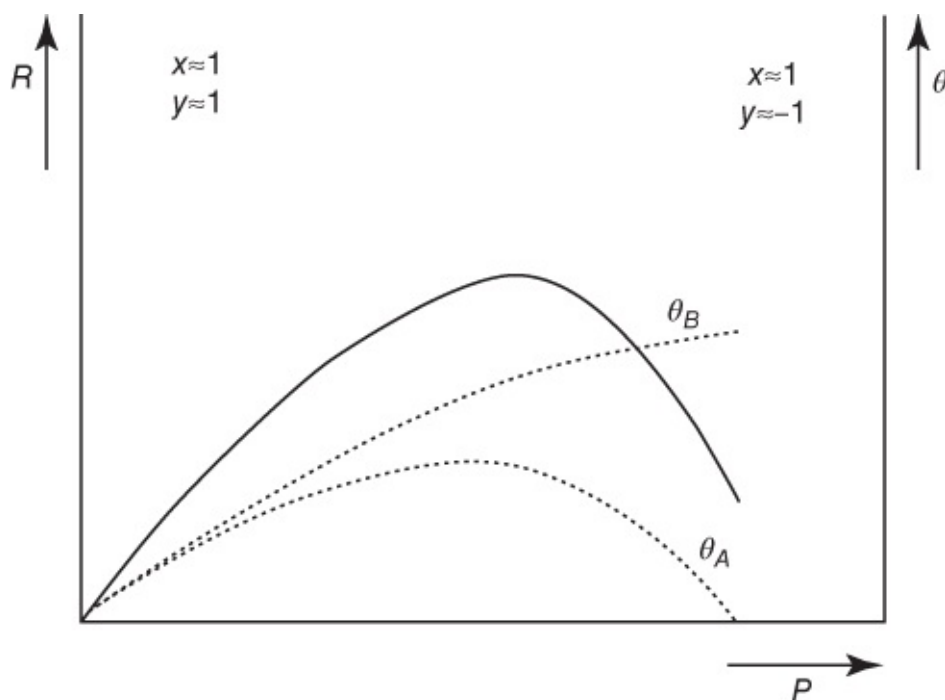


Figure 3.17 Schematic representation of change in rate R (unbroken line) with change in pressure P , with $K_{\text{ads}}^B \gg K_{\text{ads}}^A$, for a two-component reaction mixture of A and B. x and y are the exponents of $[A]$ and $[B]$ in the power law rate expression.

At low pressure, both reaction orders are positive, but while the reaction order of the component with weaker adsorption remains positive at increased pressure, it becomes negative for the component with stronger adsorption. At higher pressure, this is accompanied by dominant surface concentration of the more strongly adsorbing component that suppresses adsorption of the other component.

The relationship between surface coverage and reaction order can be readily understood by comparing Eq. (3.24a) with the Langmuir–Hinshelwood rate expression in Eq. (3.25a).

$$R_{\text{LH}} = \frac{k_r K_{\text{ads}}^A [A] \cdot K_{\text{ads}}^B [B]}{(1 + K_{\text{ads}}^A [A] + K_{\text{ads}}^B [B])^2} \quad 3.25a$$

$$R_{\text{LH}} = k_r \theta_A \theta_B \quad 3.25b$$

$$\theta_A + \theta_B + \theta_v = 1 \quad 3.25c$$

We must remember that the bimolecular LH expression is a relation determined by surface concentrations and the elementary rate constant. The LH expression can be rewritten as a power law rate expression as in Eq. (3.26), but generally has a complex form:

$$R'_{\text{PL}} \approx k_r (K_{\text{ads}}^A)^x (K_{\text{ads}}^B)^y [A]^x [B]^y \quad 3.26$$

$$(x = f(y); y = g(x))$$

The reaction orders x and y depend on surface coverages. Thus, the apparent activation energy and the reaction orders vary with surface coverages and cannot be considered independent.

Equation (3.26) will reduce to the following expressions at various limiting conditions, for example, at low surface concentration or when one adsorbed species dominates.

Representative situations are compared in Eqs. (3.27a)–(3.27c):

$$R'_{\text{LH}} \approx k_r K_{\text{ads}}^{\text{A}} (K_{\text{ads}}^{\text{B}})^{-1} [\text{A}] [\text{B}]^{-1}, \quad K_{\text{ads}}^{\text{B}} [\text{B}] \gg K_{\text{ads}}^{\text{A}} [\text{A}]; \quad \theta_{\text{A}} \ll 1; \quad \theta_{\text{B}} \approx 1 \quad \text{3.27a}$$

$$R'_{\text{PL}} = k_r (K_{\text{ads}}^{\text{A}})^x K_{\text{ads}}^{\text{B}} [\text{A}]^x [\text{B}], \quad x \approx 1 - \theta_{\text{A}}; \quad \theta_{\text{B}} \ll 1 \quad \text{3.27b}$$

$$R'_{\text{PL}} = k_r \theta_{\text{A}} (1 - \theta_{\text{A}}) = k_r \theta_{\text{B}} (1 - \theta_{\text{B}}), \quad \theta_{\text{v}} = 0 \quad \text{3.27c}$$

Equation (3.27a) gives the rate expression that corresponds to the right part of the schematic [Figure 3.17](#). One notes that k_{app} is equal to the elementary reaction rate k_r multiplied by $K_{\text{ads}}^{\text{A}}/K_{\text{ads}}^{\text{B}}$. For comparison, in Eq. (3.27b) the rate expression is given for the case where the surface coverage of component B is small and surface coverage of A varies. Now the apparent rate constant is proportional to $K_{\text{ads}}^{\text{B}}$ and $(K_{\text{ads}}^{\text{A}})^x$.

Equation (3.27c) gives the rate expression for the case where pressure is high and the surface has no vacancies. This expression shows that the rate will have a maximum related to pressure and that this maximum will occur when $\theta_{\text{A}} = \theta_{\text{B}} = 1/2$.

We will conclude with an example of a competitive adsorption reaction as a function of reactant mixture concentration changes. The ring-opening reaction of methylcyclopentane to give linear and branched alkanes is this type of reaction, catalyzed by Pt. We will study its rate as a function of H_2/HC ratio.

As [Figure 3.18](#) shows, the rate of hydrogenation has a maximum as a function of the H_2/MCP partial pressure ratio.

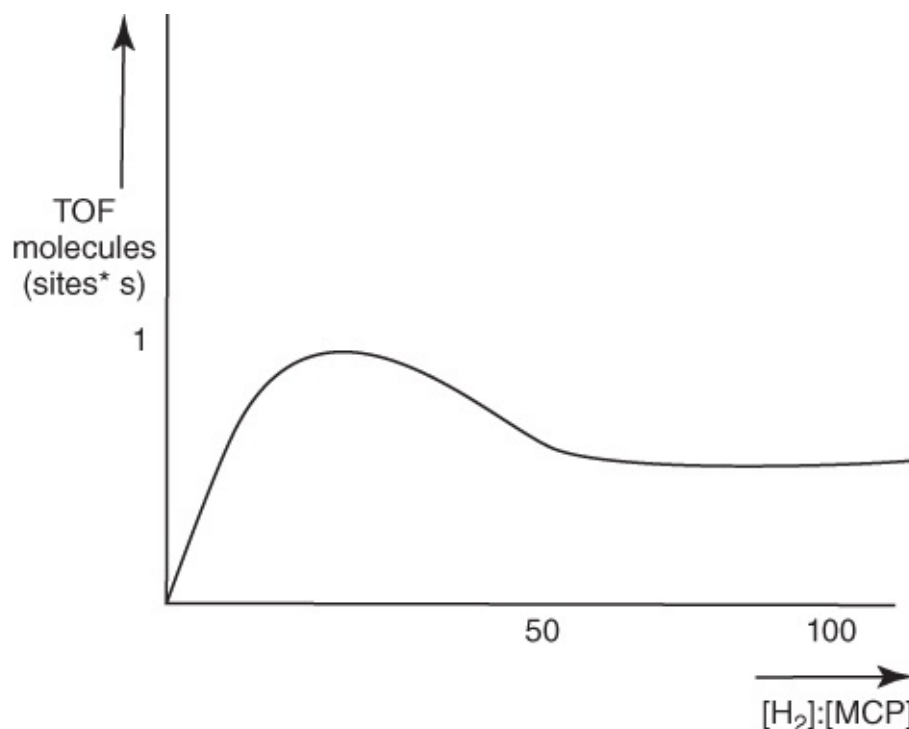


Figure 3.18 Activity of the ring opening of methyl cyclopentane as a function of $[H_2]/[MCP]$ for platinum supported on Al_2O_3 (schematic). (After [35].) (See also [36].)

At low hydrogen partial pressure, there is an expected positive order in hydrogen because H_2 is needed for the reaction. At high partial pressure of hydrogen, the reaction rate becomes negative order in H_2 , because the adsorption of hydrogen now suppresses olefin adsorption. The positive order of hydrogen at low partial pressure can also be partially due to the need for removing catalyst-deactivating carbonaceous residue formed at low hydrogen pressure.

The dependence of reaction order on condition implies that the order may be very different when partial and total pressures or temperature is varied. For this reason, attempts to deduce mechanistic information from reaction orders have only limited value. Reaction rate expressions based on parameters derived by experiment can only be applied within the reaction condition regime where they were determined and have no *a priori* predictive value outside this regime.

3.4 Transient Kinetics: The Determination of Site Concentration

The kinetic expressions predict a rate of reaction that is proportional to the number of catalytically reactive sites. This prediction is valid only as long as diffusion does not limit the transport from the reagent phase to the catalytically reactive site, which is the condition of intrinsic kinetics. When diffusion is limiting, we must consider extrinsic kinetics that accounts for diffusion. This will be discussed in the next section. The rate of reaction normalized to the number of reactive surface atoms and expressed as the number of molecules converted per unit of time is called the **turnover frequency**.

For a practical catalyst, the actual fraction of catalytically active sites on a reactive surface is rarely known. This fraction can be quite small compared to the total number of exposed surface atoms. This is because the catalytic reactivity may also be a strong function of the surface topology of the reaction center. Practical catalysts will have a distribution of different surface structures exposed, and this distribution sometimes relates to the distribution of particle size of the reactive particles.

As long as intrinsic kinetics apply, transient kinetic measurements in combination with steady state kinetics can be used to decouple the kinetics of the reaction from the number of sites.

Since the surface state of the catalyst depends on reaction conditions that are not necessarily maintained after the reaction, the number of reaction centers must be determined during the reaction by a so-called *in situ* experiment. A chemical probe used for this purpose is an isotope switch in the reagent. This has only a small effect on the chemistry of the reaction (when H/D exchange is used, the activation energies are slightly altered), so that the TOF is not essentially affected.

Such an isotope switch event is schematically illustrated in [Figure 3.19](#) for the CO hydrogenation reaction to methane.

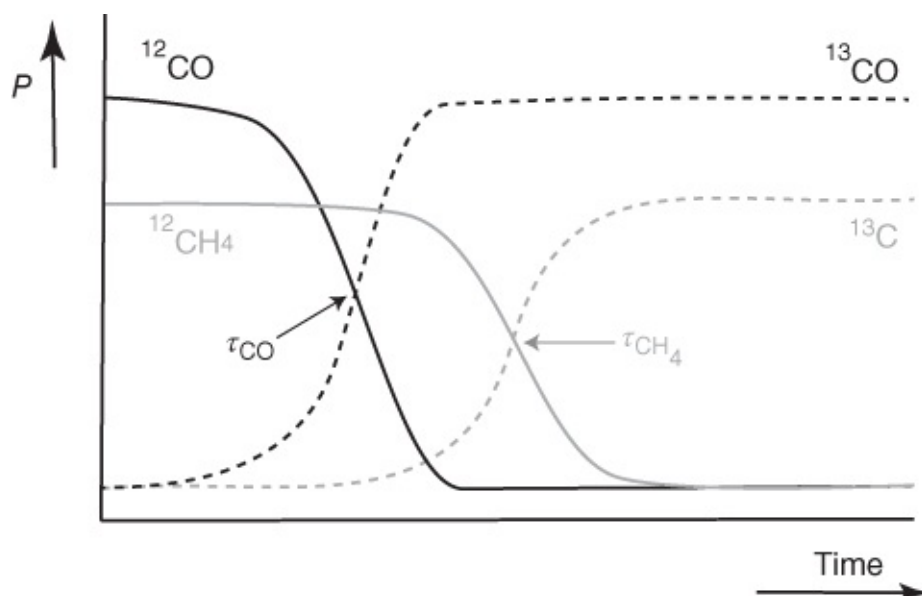


Figure 3.19 Example of transient behavior for CO methanation following an isotope switch, illustrating how residence half-lives and surface coverages change.

For reactions that include an isotope-switch event, a plug flow reactor is used at conditions of minimized back-mixing. When the reaction is at steady state, a reagent molecule is switched to its isotope. The rate of disappearance of the non-labeled reagent and product molecule and the appearance of labeled product is tracked by mass spectroscopy.

In the example of the CO to methane reaction, ^{12}CO can be switched to ^{13}CO and the $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ product concentrations are followed as a function of time. The concentrations of labeled and non-labeled products will decrease exponentially with time. In addition, an inert gas is usually injected and the response times of product molecule and inert gas are

compared. This helps to determine the time constant of the reactor that must be subtracted from the transient product signal.

The response times τ_x are independent of the number of reactive centers. In the example in [Figure 3.19](#), τ_{CO} measures the replacement of ^{12}CO by ^{13}CO . This is determined by the inverse of the rate constant of CO desorption $k_{\text{des,CO}}^{-1}$, as long as the equilibration of CO between the gas phase and the surface is fast compared to the rate of reaction R . The rate of replacement of CH_4 by its isotope-labeled product is different, and given by the inverse of the rate of CH_4 production normalized per site, which is equal to the TOF^{-1} . Once the rate per site is known the number of sites N_s can be calculated since the overall rate of methane production is given by $R_{\text{CH}_4} = N_s \cdot \text{TOF}$.

The relation between τ and the elementary reaction rates depends on the rate-controlling step. When the rate constant of CO dissociation is rate controlling, τ_{CH_4} is determined by the rate of CO dissociation, but when hydrogenation of adsorbed C atoms is rate-controlling it is determined by the rate of C_{ads} removal.

Steady-state isotopic-transient kinetic analysis (SSITKA) measurements can only be useful as long as diffusion is fast. This prevents their application to microporous systems where pore diffusion becomes a significant factor.

3.5 Diffusion

3.5.1 Concentration Profiles

Heterogeneous catalysts are porous particles with a high internal surface area. The catalytically reactive particles are distributed over this internal surface. Molecules require time to travel the length of the pores to reach the catalytically reactive particles and surfaces. This causes a gradient in the concentration of reacting molecules across the micropores when the rate of reaction is fast compared to the diffusion rate. The time of diffusion τ_D needed to traverse the micropores is compared with the reaction time τ_R , of intrinsic kinetics, equal to R_i^{-1} . As the following equations illustrate, diffusion becomes limiting when the reaction rate is fast, the micropore is long, and the diffusion coefficient is small.

The diffusion time τ_D is given by the Einstein relation:

$$L^2 = 2D\tau_D \quad 3.28$$

L is the length of the micropore and D is the diffusion constant. Diffusion becomes relevant when:

$$\tau_D = \frac{L^2}{2D} > \tau_R = \frac{1}{R_i} \quad 3.29$$

R_i is the intrinsic rate constant in the absence of diffusion-limitation.

The time τ_r of catalytic reaction must be small compared to the diffusion time τ_D required to reach the reactive center. Diffusion may be expected to be important at high temperatures when the rate of reaction is also high.

The relation shown in Eq. (3.28) is valid for the case of Knudsen diffusion. The rate of diffusion is determined by collisions with other molecules, and thus the activation energy of diffusion will be low compared to that of a chemical reaction. Differences in diffusion rates are related to the mass of the particles by $\frac{1}{\sqrt{m}}$ (since $(1/2)mv^2 = (3/2)kT$).

When the size of the molecule equals the size of the micropore, the diffusion rate is dominated by collisions with the pore wall. This is exhibited in the micropores of zeolitic systems, which we will discuss in [Section 3.5.3](#).

3.5.2 Effectiveness Factor

Diffusion will limit the overall rate of a reaction, and this is represented by an inhibiting factor called the **effectiveness factor** η_f . The expression for the overall rate of the reaction R_d when diffusion is limiting becomes:

$$R_d = \eta_f R_i \quad 3.30a$$

For a spherical particle the effectiveness factor η_f is related to the Thiele modulus ϕ_t [1].

$$\eta_f = \frac{3}{\phi_t} \left[\frac{1}{\tanh \phi_t} - \frac{1}{\phi_t} \right] \quad 3.30b$$

For a monomolecular reaction whose rate is diffusion-limited ($L^2/D \gg 1/R_i$), the expression for the effectiveness factor η_f reduces to:

$$\eta_f \approx \frac{1}{\phi_t} = \left(\frac{2D}{L^2 R_i} \right)^{1/2} \quad 3.31$$

Insert 3.8 gives an insightful derivation of this expression.

Insert 8 Effectiveness Factor Derivation and Diffusion-Related Change of Apparent Activation Energy

Derivation of Effectiveness Factor for Monomolecular Reaction

A simple heuristic argument can be used to deduce an expression for the Thiele modulus (after [3]). When pore diffusion is limiting, the rate of product formation is given by

$$\frac{d[P]}{dt} \approx R_d[c_0]L \quad 8i.1$$

$[c_0]$ is the concentration of reagent at the pore mouth, which by diffusion becomes distributed over the pore of length L .

Since reaction is diffusion-limited, instead of the inequality in Eq. (3.29), the equality in Eq. (8i.2) applies:

$$\frac{L^2}{2D} = \frac{1}{R_i} \quad 8i.2$$

L can be substituted into Eq. (8i.1) to give

$$\begin{aligned} \frac{d[P]}{dt} &\approx R_i[c_0]L \sqrt{\frac{2D}{R_i L^2}} \\ &= R_d[c_0]L \end{aligned} \quad 8i.3$$

The effectiveness factor follows from the comparison of Eq. (8i.3) with Eq. (3.30a).

The Apparent Activation Energy Change by Diffusion Equation (34) leads to the conclusion that when a reaction becomes diffusion-limited the apparent activation energy E_{app} becomes half of the apparent activation energy of the intrinsic (not controlled by diffusion) activation energy E_{app}^{intr} . The rate of reaction also becomes proportional $\sqrt{N_c}$ instead of being linearly dependent on the number of active sites N_c . The apparent activation energy as a function of temperature is shown in Figure 8i.1.

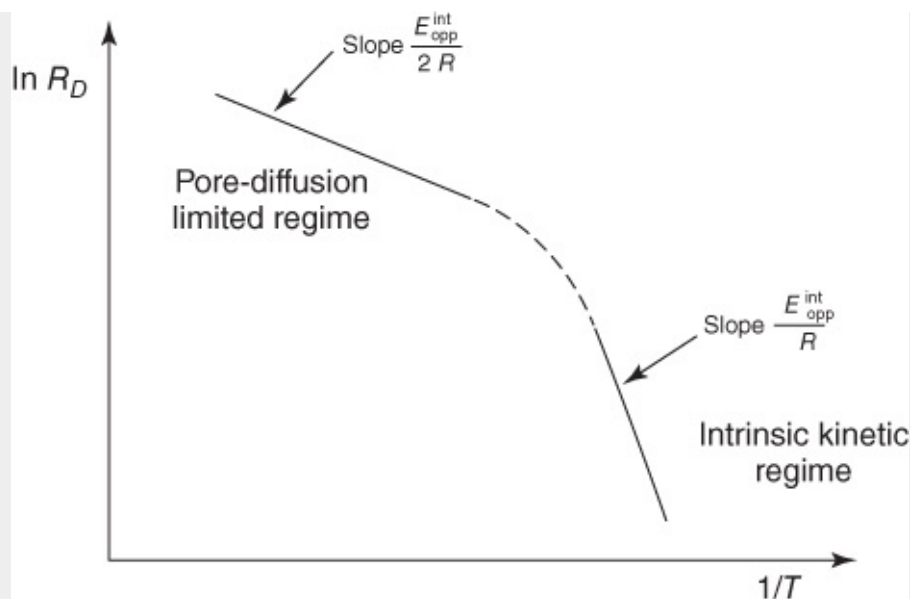


Figure 8i.1 Illustration of the change in activation energy for a reaction that becomes limited by diffusion at high temperature.

From Eqs. (3.31) and (3.30a), the expression for the diffusion-limited rate of the reaction R_d becomes:

$$R_d = \sqrt{\frac{2D \cdot R_i}{L^2}} \quad 3.32$$

Interestingly, we see in Eq. (3.33) for the diffusion-limited rate that the apparent rate now depends on the square root of the intrinsic apparent activation energy. Therefore, the apparent activation energy for the diffusion-limited case E_{app}^d now becomes half of that of the apparent activation energy that is not diffusion-limited:

$$E_{app}^d = \frac{1}{2} E_{app}^{intr} \quad 3.33$$

When the rate of a reaction catalyzed by porous materials is studied as a function of increasing temperature, it may change from non-diffusion-limited to diffusion-limited. Consider the case where, at a low temperature, the rate of reaction is slow and therefore not diffusion-limited. When temperature increases, the rate of reaction also increases and may reach a point where diffusion becomes limiting. The activation energy at high temperature is half that of the activation energy at low temperature, as illustrated in Figure 8i.1.

Experimentally, the decrease in the activation energy of a reaction cannot be considered proof that the reaction is pore diffusion-limited, because even when the catalytic reaction is not diffusion-limited the intrinsic apparent activation energy of the reaction rate may decrease with temperature. This is due to the change in surface concentrations which will affect intrinsic kinetics (see Figure 3.16).

A hallmark of pore diffusion-limitation is the change in rate of reaction when catalyst particle size changes. Because the effectiveness factor depends on pore length, the rate of the diffusion-limited reaction will be affected, but if reaction rate is non-mass transfer limited it will remain unchanged.

Pore diffusion may also change the relative concentration of a gas mixture as a function of pore depth, because of differences in diffusion constant. A heavy molecule has a smaller diffusion constant than a lighter one. This is important in hydrogenation reactions where the hydrogen partial pressure will increase deeper in the pore due to the higher diffusion constant of H_2 .

Pore diffusion may affect not only the conversion rate, but also the selectivity of a reaction. If the desired product of a reaction is an intermediate that must not be converted by consecutive reaction steps, this intermediate should be quickly removed from the neighborhood of the reactive center. Since pore diffusion-limitation will limit the rate at which the intermediate product molecule is moved out of the catalyst pore, it will reduce the selectivity of the reaction. The increase of the residence time of the intermediate product in the pore will increase its conversion rate.

An example of this scenario is selective oxidation, where the undesirable consecutive reaction is the total combustion of the initially formed product. For this reason, selective oxidation reactions are catalyzed using catalysts with low pore volume. This must be balanced against the need for enough surface area to achieve an acceptable overall rate of reaction.

In the case of the Fischer–Tropsch reaction (see [Section 2.2.3.2](#)) the diffusion constant of H_2 is substantially faster than that of CO. This increases the relative hydrogen concentration deep in the catalysts pore, which will increase the relative rate of undesirable light gas formation by enhancing the rate at which adsorbed hydrocarbon intermediates will become hydrogenated and desorb from the catalyst surface.

When the rate of reaction becomes so fast that a concentration depletion layer of reagent molecules forms around the catalyst particle, the overall rate of reaction is controlled by the diffusion of molecules through this layer. This is called **film diffusion**, and it can occur in reactions at very high temperature or in electro-catalytic reactions at low temperature in the liquid phase. The apparent activation energy of the reaction is then equal to the activation energy of molecular diffusion on the order of only a few kilojoules per mole. One way to verify these interphase concentration or related temperature effects is to vary the space velocity of reactor feed streams using a constant contact time. This can be done by adjusting the amount of catalyst material in the reactor. Film diffusion will cause the observed rate of reaction to change with space velocity. (For a more in-depth discussion refer to Dautzenberg [13].)

3.5.3 Diffusion in Zeolitic Micropores

Unlike Knudsen diffusion, diffusion of molecules in a microporous zeolite does not

necessarily depend on the mass of the molecules that diffuse. When the radii of molecules and micropores match closely and the micropore wall is smooth (e.g., in a linear pore) the diffusion constant may become independent of molecular mass. For instance, in the siliceous mordenite zeolite ([Figure 3.20](#)) that has linear micropores, diffusion of alkanes becomes independent of alkane chain length and much faster than expected from Knudsen diffusion estimates. Diffusion in this case can be considered to be floating diffusion ([Figure 3.20](#)).

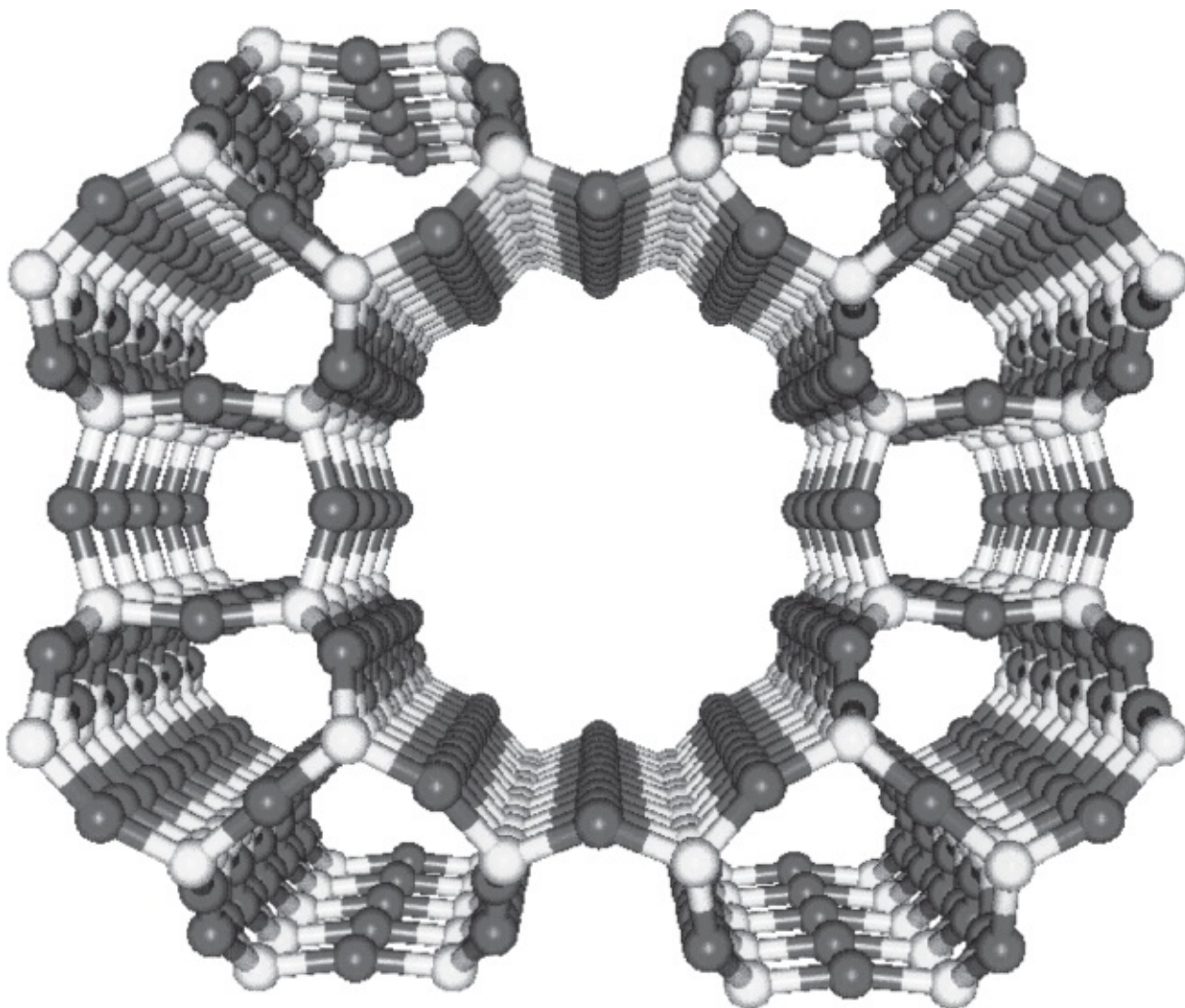


Figure 3.20 Zeolite mordenite structure.

The adsorption energy of hydrocarbons with the siliceous wall of the zeolite occurs by physical adsorption. This interaction is based on the dispersive interaction between molecules and zeolite channel atoms, and is proportional to the polarizability of the atoms that are in contact. In the zeolite, this is dominated by the interaction with large oxygen atoms: the polarizability is proportional to the volume of an atom, and is hence dominated by the larger O anions with little contribution from the smaller cations. The interaction is linear in the number of alkane CH₂ units. It is on the order of 5–10 kJ mol⁻¹ per CH₂ unit in contact with a zeolite wall O atom, but decreases when the microchannel chain radius increases. While the adsorption energy increases linearly with alkane length, the diffusion constant remains independent because the area of contact with the zeolite wall does not change.

[Figure 3.21a](#) illustrates the independence between the diffusion constant and the length of the hydrocarbons for hydrocarbons of varying length. The importance of the topology of the micropore structure and the shape of the microcavities is illustrated by [Figure 3.21b](#) for the faujasite structure. The faujasite structure is three-dimensional and contains large cavities. The average distance between the molecules and the zeolite wall is larger and floating diffusion is absent. The simulated diffusion constants now decrease with the increasing mass of the alkanes. The diffusion rate of molecules in the micropores of a zeolite can vary substantially as a function of micropore filling. Yet, the diffusion time through the inter-crystallite space of the zeolite that consists of the larger meso- and micropores is often longer than the diffusion time through the smaller zeolite micropores. This is because the inter-crystal pores are longer and have a larger relative volume than the micropores of the small zeolite particles.

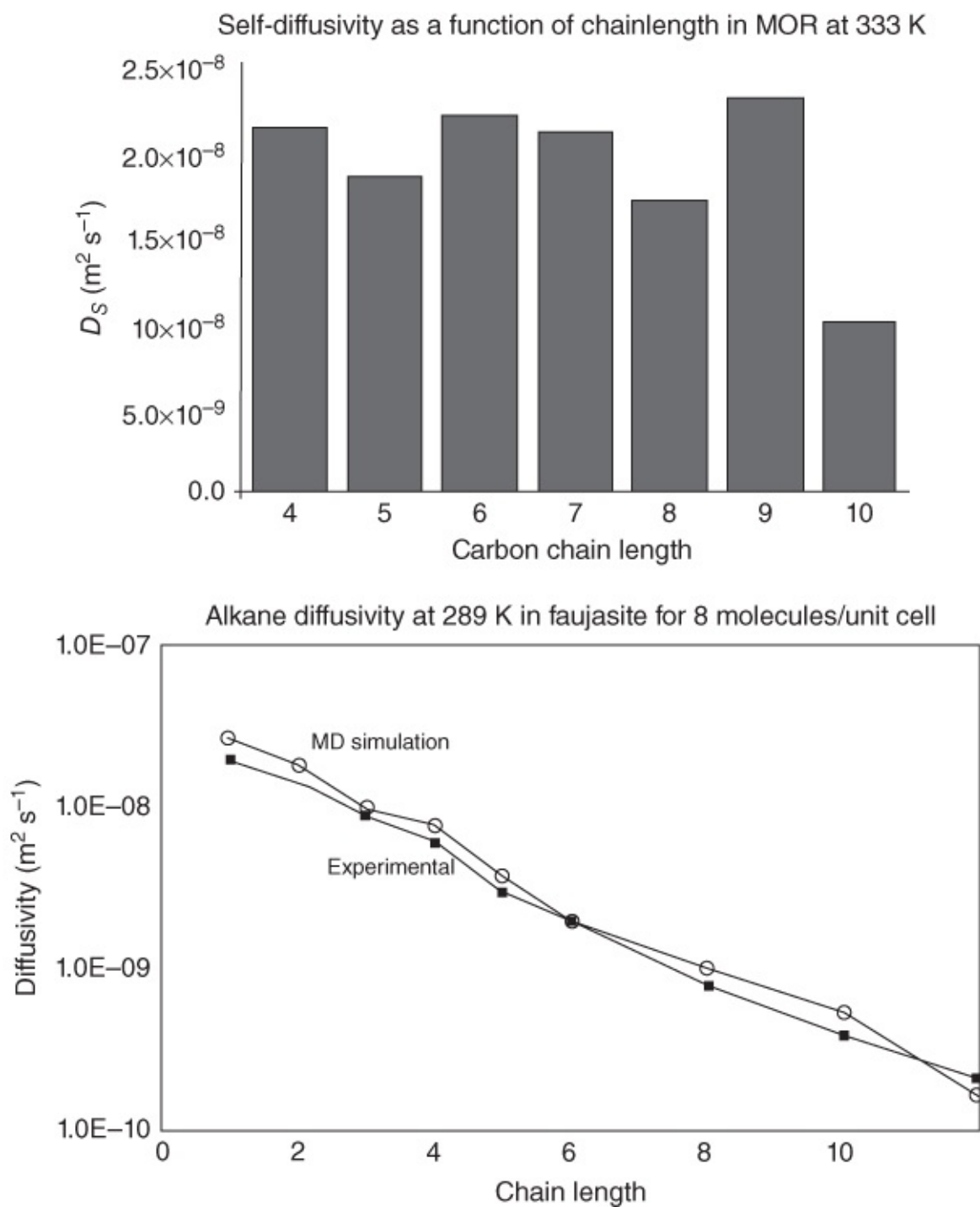


Figure 3.21 (a) Self-diffusivity as a function of chain length in siliceous mordenite at 333 K. (b) Simulated diffusion constants in siliceous faujasite as a function of hydrocarbon chain length. (After [9, 37].)

The interaction of hydrocarbons with the zeolite micropore wall is surprisingly strong, despite the fact that it is based on weak physical dispersive van der Waals interactions. It increases linearly with the number of CH_2 units. For a narrow pore siliceous zeolite with a 10-ring channel diameter such as Ferrierite, the adsorption energy of hexane is 60 kJ mol^{-1} . This is because in the small zeolite micropore the hydrocarbon CH_2 unit makes contact with several O atoms.

This can cause high hydrocarbon occupation of the micropores when high pressure of reaction is used at relatively low temperatures. The diffusion rate decreases because the mobility of molecules is hindered by the presence of co-adsorbed molecules. Equilibration of the reaction intermediates within the micropore becomes fast compared to the equilibration with the external reaction medium outside the zeolite. Selectivity of the reactions is then determined by the adsorption-free energies of reaction intermediates within the micropores. There is a bias for the formation of molecules with a shape that can be adapted to the shape of a particular zeolite micropore (for instance, linear molecules are favored in the case of linear microchannels). The result is shape-selective catalysis. We will discuss this in detail in [Sections 9.2](#) and [9.3](#).

Another cause of shape-selective catalysis is when molecules are too large to enter the microcavities of the zeolite; in a mixture of molecules with different sizes, only the smaller molecules will be converted. This size restriction also prevents the formation of reaction intermediates that are too large to be accommodated in the micropores. We described this phenomenon earlier for the suppression of coke formation in the catalytic cracking reaction, where formation of large aromatic molecules is suppressed by the size of the zeolite micropores.

When cations are located in the zeolite channels, their high electrostatic field may cause relatively high adsorption energies for polarizable molecules or molecules with a large dipole moment. In this case, diffusional motion depends strongly on temperature. For instance, in zeolites exchanged with earth alkali cations strong sieving is observed for mixtures of benzene and hexane. The polarizable benzene molecule will adsorb strongly and therefore diffuse slowly, but the hexane molecule will have a high diffusion constant.

A unique phenomenon that occurs at high micropore occupation in the narrow one-dimensional micropores of a zeolite is single-file diffusion. The small micropore size restricts the passage of molecules. This is important in hydroisomerization catalysis where the preferred catalyst is mordenite which contains narrow one-dimensional micropores of a diameter comparable to that of linear hydrocarbons (Section 2.2.2.1.3). Mobility is possible only when all molecules that have no vacant position between them displace at the same time. The number of molecules in a file is at its maximum when it fills the zeolite micropore between two catalytically reactive centers. Its dependence on pore occupation θ is [38, 39]:

$$D_s = D_0 \frac{1 - \theta}{\theta} \frac{l}{L} \quad 3.34$$

D_0 is the self-diffusion constant of a single particle and θ the partial occupancy of the pore, L is the length of the pore, and l is the average distance between the catalytic reaction centers in the micropore.

Single-file diffusion leads to a specific relationship between the rate of reaction and the partial pressure of reagent molecules [40].

The kinetics of the hydroisomerization reaction catalyzed by the bifunctional Pt-promoted

mordenite zeolite can be approximately described by the lumped kinetics expression of the monomolecular reaction in Eqs. (3.14). As a function of partial pressure of the alkane, the rate will have a Langmuir-type dependence on pressure. For regular micropore diffusion, the intrinsic rate shown by Eqs. (3.14a) and (3.14b) will depend on the effectiveness factor η_f (Eq. (3.31)), as illustrated in Figure 3.22.

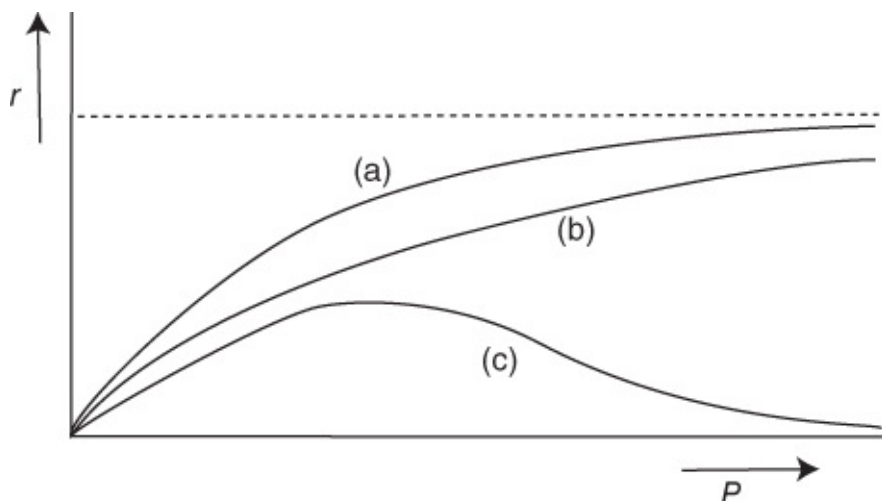


Figure 3.22 (a) The rate of a monomolecular zeolite-catalyzed reaction as a function of pressure (no diffusional limitation). (b) The rate of the monomolecular reaction that is diffusion-limited (pore diffusion, no single-file diffusion). (c) The rate of a monomolecular reaction that is limited by single-file diffusion. (van Santen and Neurock 2006 [9]. Reproduced with permission of John Wiley & Sons.)

Pore diffusion will cause a deviation from the Langmuir-type partial pressure dependence, but the rate will still monotonically increase with partial pressure of alkane. This is not the case for single-file diffusion. Instead, the apparent diffusion constant becomes zero at high coverage, and the rate shows a maximum as a function of partial pressure with a subsequent decrease at high pressure.

In principle, small zeolite crystallites can be used to minimize this strong diffusional resistance, but this is not realized in practice. Instead, catalyst activity is improved by creating mesoporous channels within the zeolite crystallite, so that the effective micropore channel length decreases and the transport of molecules becomes efficient. These channels can be created by partial leaching of Al present in the mordenite crystals that are synthesized with a high Al/Si ratio.

In catalytic reactions, the use of such bimodal porous zeolitic systems containing a combination of mesoporous and microporous channels is also effective for reducing the rate of deactivation that is caused by zeolitic micropore blockage because the mesochannels allow a larger fraction of the zeolite particle interior to remain accessible.

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