

2

Concepts

Adsorption of atoms or molecules from their vapor phase to a solid surface occurs when attractive forces act at short distance between them. Depending on the magnitude and origin of these attractive forces and the extent of perturbation to the respective electronic structures, the phenomenon of adsorption is broadly classified into two types: physisorption and chemisorption [Adamson, 1982]. The attractive forces in physisorption originate from correlated charge fluctuations that develop when an atom or a molecule is brought into the vicinity of a solid surface. These attractive forces are van der Waals (vdW) forces. The physisorption of molecules or atoms on a solid surface is characterized by largely unperturbed electronic structures of both the adsorbate and the surface. Adsorption of noble gas atoms on metal surfaces is a typical example of physisorption. On the other hand, the forces that are responsible for chemisorption arise from the overlap of adsorbate and surface wave functions. This wave-function overlap leads to the formation of new bonds and thus a modification of their electronic structures. The rupture of intramolecular adsorbate bonds and the formation of new surface bonds during chemisorption are crucial steps in any heterogeneous catalysis. The chemisorption of oxygen on carbon surfaces is a focal point of this thesis.

The desorption of an adsorbed species from a surface is considered to be the reverse process of adsorption. Therefore, the rate of desorption can be used to obtain the energetics and type of adsorption [Ageev and Ionov, 1975]. Also, using the principle of detailed balance between the adsorption and desorption, it is possible to derive desorption parameters such as pre-exponential frequency factors, orders of desorption, etc., from the thermal desorption data [Ageev and Ionov, 1975; Christmann, 1991].

This chapter will provide a conceptual introduction to the phenomena of physisorption and chemisorption. Both can be microscopically understood in terms of interaction potentials as adsorbates are brought near a solid surface.

2.1. Physisorption

The physisorption of a gas-phase molecule on a solid surface arises from the attractive vdW interactions that are developed when the gas molecule is brought near the solid surface. The cause of this attractive interaction is the quantum mechanical fluctuation of instantaneous dipoles, which originates from the mutual interaction of electrons in the adsorbate and the surface.

2.1.1. Energetics of physisorption

A simplistic model of the process leading to physisorption is shown in Fig. 2.1. Here, a neutral atom with a single valence electron is depicted approaching a semi-infinite solid surface with a dielectric constant ϵ [Jackson, 1999; Lüth, 2001].

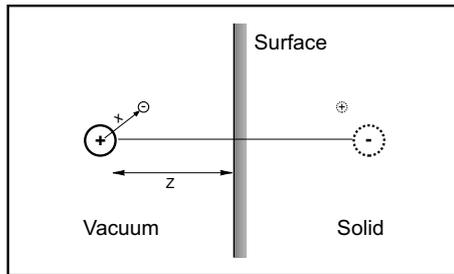


Figure 2.1.: Schematic illustration of image state when an atom approaches the surface of solid. Here the atom and the single electron are considered as point charges. The attractive and repulsive forces that lead to physisorption can be explained in terms of the interactions between the point charges and their images.

potential $V(z)$ corresponding to above attractive forces, can be shown to have an asymptotic dependence on the distance of the atom from the surface, z . This potential increases asymptotically as the atom approaches the surface and is given by $V(z) \propto -z^{-3}$ [Zaremba and Kohn, 1976]. However, as the atom is brought very close to the surface, the overlapping wave functions of the atom and the surface lead to increased kinetic-energy components of the electrons. This leads to a high repulsion potential [Zaremba and Kohn, 1977]. A physisorbed state is attained by

The interaction of the point charge, $+e$ from the nucleus, with the surface induces an image point charge q [Zangwill, 1988],

$$q = \frac{1 - \epsilon}{1 + \epsilon} e, \quad (2.1)$$

which is positioned within the solid at the same distance from the surface. Similarly, the interaction of the valence electron ($-e$) induces a corresponding image point charge. This system of point charges and their images constitute the induced dipoles, and are responsible for the attractive forces (vdW forces) that arise when the atom is brought near the surface.

Modeling the electronic motion in atoms as simple Lorentz oscillator, the attractive

the balance between the above attractive and repulsive forces. A physisorption potential is represented by the sum of the repulsive and attractive van der Waals contributions as shown in Fig. 2.2.

Solids whose cohesion is driven by vdW forces, i.e., the van der Waals bonded solids, attain their equilibrium geometry by having a balance between these attractive and repulsive forces. This comparison between the van der Waals bonded solids and physisorbed gases on solids can be used to derive the van der Waals interaction within the solids themselves. The interactions that lead to physisorption are universal, i.e., the attractive and repulsive forces are experienced by even neutral moieties without permanent dipole moments, as a species is brought near the surface. The physisorption potentials are characterized by a low binding energy (depth of the potential well in Fig. 2.2), which is on the order of 10 to 300 meV, and by a relatively large equilibrium separation, about 3–10 Å [Lüth, 2001; Vidali et al., 1991].

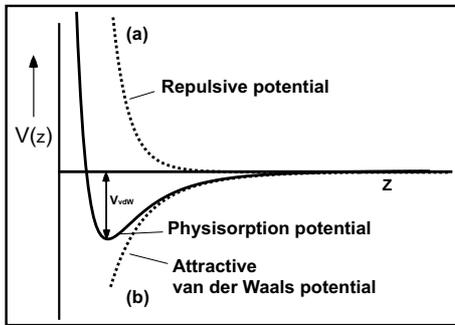


Figure 2.2.: One-dimensional potential energy diagram corresponding to physisorption of neutral atoms or molecules on surfaces (solid line). Broken lines represent (a) the van der Waals attractive potential which is dominant at larger separation z and (b) the repulsive potential due to the overlap of electronic wave functions which is dominant at shorter distances.

with no significant electron density between them. So far, only the dispersive contribution (V_d) of the attractive van der Waals potential is considered. This has been justified when studying the interactions between a neutral molecule with a permanent dipole moment. For studying the interaction of polar molecules, a complete description of the van der Waals interaction has contributions from orientational (V_o) and induction terms (V_i) [Israelachvili, 1992]:

$$V_{vdW} = V_d + V_o + V_i.$$

The theoretical calculation of van der Waals interaction potentials has produced a large range of values. It has been mentioned that the even most modern theoretical techniques are not adequate to obtain reliable results. A classic example of this are sparse systems, i.e., systems in which vdW interactions are dominant to covalent interactions [Kohn et al., 1998; Rydberg et al., 2003]. Graphite, whose interlayer cohesive energy is studied in chapter 4, is considered as a good example of a sp^2 bonded sparse system. The van der Waals interaction potential in a physisorption system and covalently bonded solids such as graphite can be obtained experimentally from the thermal desorption (TD) data.

2.1.2. Desorption of physisorbed species

The macroscopic description of physisorption for gas-phase molecules on a solid surface models the surface concentration of the adsorbate as a function of equilibrium gas pressure. For a simple physisorption system, the relation between surface concentration of the adsorbate and the gas pressure is given by the Langmuir adsorption isotherm:

$$\theta = \frac{bp}{1 + bp}, \quad (2.2)$$

where θ is the surface coverage expressed in monolayers, and b is a temperature dependent constant given by:

$$b = \frac{s_0}{\nu\sqrt{2\pi mk_B T}} \exp\left(\frac{E_d}{k_B T}\right). \quad (2.3)$$

Here s_0 is the sticking probability ($0 \leq s_0 \leq 1$), m is the mass of the adsorbate molecule, ν is the pre-exponential frequency factor for desorption and E_d is the activation energy for desorption. The relationship shown in Eq. (2.2) is derived with the following assumptions: (1) adsorption on specific sites, (2) adsorption capacity is exhausted after a saturated monolayer ($\theta = 1$), and (3) there is no lateral interaction between neighboring adsorbate molecules. However, above assumptions are not valid for all physisorption systems; at large surface coverages, interactions between adsorbates is observed in many physisorption systems. In addition, the exposure of a surface to gas molecules at sufficiently low temperature results in the growth of multilayers of adsorbents. The formation of mono- or multilayer of adsorbents depend on the magnitudes of adsorbent-adsorbent and adsorbent-surface interactions. The relative strength of these interactions provide three different models for the growth of adsorbates: Frank-van der Merve, Vollmer-Weber and Stranski-Krastanov growth models (Fig. 2.3). They are defined below:

- Frank-van der Merve (*layer-by-layer*) growth: In this model of adsorbate growth, each new layer starts to grow only after the underlying layer is complete. This type of growth occurs when the interaction between the adsorbate

and the surface is stronger than that between the adsorbates. A schematic illustration of the Frank-van der Merve model of adsorbate growth as a function of surface coverage is shown in Fig. 2.3(a).

- Vollmer-Weber (*island*) growth model: This is opposite to the first model and occurs when the interaction between adsorbate molecules is stronger than those between the adsorbate and the substrate. Consequently, the adsorbate forms multilayer conglomerates [Fig. 2.3(b)].
- Stranski-Krastanov growth: This is a mixed mode of adsorbate growth in the sense that the formation of both the islands and complete monolayers are observed. Here, after the formation of one or two complete monolayers, island formation occurs [Fig. 2.3(c)]. The nature of the adsorbate layer is dependent not only on the relative strength of binding between the adsorbate and the substrate, but also on other parameters such as lattice mismatch and orientational effects of overlayers [Lüth, 2001]. Growth of rare gases on graphite usually follow this growth pattern.

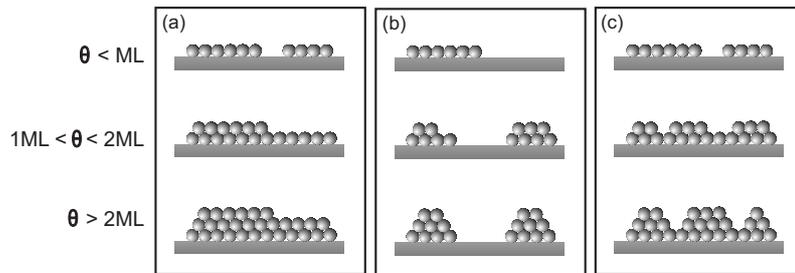


Figure 2.3.: Schematic representation of the three growth modes during physisorption at different coverage regimes. (a) Layer-by-layer growth or Frank-van der Merve mode, (b) island growth or Vollmer-Weber mode and (c) mixed or Stranski-Krastanov mode. The coverages θ are indicated in units of monolayers (MLs).

The binding energy of the adsorbate molecule as it approaches the surface (Fig. 2.2) can be obtained from the rate of adsorbate desorption in the above depicted mono- and multilayers. This rate of desorption is given by the Arrhenius rate equation:

$$-\frac{d\theta}{dt} = \nu\theta^n \exp\left(-\frac{E_d}{k_B T}\right). \quad (2.4)$$

Here ν is the pre-exponential frequency factor and E_d is the activation energy of desorption. Since physisorption is generally a non-activated process, the activation energy of desorption is equal to the binding energy of the adsorbate to the surface, i.e., $E_d = E_b$ (see Figs. 2.5).

2.1.3. Desorption from porous carbon surfaces

In the previous section where the desorption from a solid surface is presented, it was assumed that the solid surface is a non-porous single crystal without inhomogeneities. The thermal desorption spectrum of gas molecules from porous substrates, such as SWNT bundles or carbon nanofibers, cannot be entirely accounted by the Arrhenius equation.

The thermal desorption of adsorbates from porous surfaces occurs at higher temperatures and have a wider temperature range than that expected from Arrhenius kinetics [Ulbricht, 2003]. The three most important reasons that can be responsible for the broadening of TD spectra are: (1) the slow kinetics due to the dominant diffusion processes inside the void spaces of porous carbon samples, (2) inhomogeneity due to the impurities and (3) inhomogeneity due to the defects. In the below, the contribution due to diffusion processes are presented using coupled desorption-diffusion (CDD) model [Ulbricht et al., 2002a].

A comparison of the density of bucky paper used for typical thermal desorption experiments and that of single-wall nanotube (SWNT) bundles reveals that about 60% of the sample volume consists of empty spaces in the form of pores or cavities. Therefore, in such highly porous samples, the complete mass transport equations modeling the desorption has additional terms arising from the diffusion within the pores [Ulbricht et al., 2002a]. In order to accurately account for these thermal desorption features, it is necessary to couple the mass transport from diffusion to that of desorption. In the CDD model, the total mass transport during desorption experiments are accounted for by three contributions: (1) desorption from the visible surfaces, (2) diffusion within the internal sample surfaces and (3) diffusion of the gas species that have been desorbed from the internal spaces until they come into contact with the surface. The last type of diffusion is referred to as Knudsen type diffusion (see Fig. 2.4). The contribution of the adsorbate concentration moving perpendicular to the surface because of the diffusion processes is given by [Ulbricht et al., 2002a]:

$$\frac{\partial C(z)}{\partial t} = \{D_g h(T) + D_s [1 - h(T)]\} \frac{\partial^2 C(z)}{\partial z^2}, \quad (2.5)$$

where $C(z)$ is the concentration of the adsorbent perpendicular to the surface, D_g is the Knudsen type diffusion coefficient and D_s is the surface diffusion coefficient. $h(T)$ is a kinetic term and is represented by:

$$h(T) = \left(1 + \frac{k_B T b A_s}{f \sigma}\right)^{-1}. \quad (2.6)$$

Here A_s is the specific surface area per volume, σ is the number of molecules per unit surface area and f accounts for the fraction of void volume of the sample. b is a constant which is obtained from the Langmuir adsorption kinetics and is given

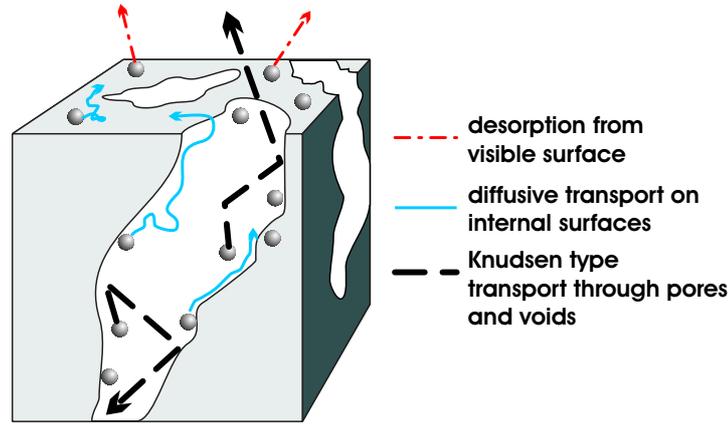


Figure 2.4.: Schematic illustration of three modes of transport: desorption, surface diffusion and Knudsen type transport in a porous structure.

by:

$$b = \frac{s_0}{\nu \sqrt{2\pi m k_B T}} \exp\left(\frac{E_d}{k_B T}\right), \quad (2.7)$$

where m is the adsorbate mass, E_d is the activation energy for desorption and ν is the frequency factor.

The one-dimensional gas-surface diffusion equation [Eq. (2.5)] can be solved numerically to obtain the contribution from the diffusion processes to the adsorbate concentration profile. For the thermal desorption of Xe from SWNT-bundles, the solution of Eq. (2.5) is shown to account very well for the broadening of the TD spectra, if mass transport is dominated by gas-phase diffusion [Ulbricht et al., 2002a]. This is equivalent to the condition that $(E_d - E_m) < 2.3nk_B T$, where E_m is the rate-limiting surface migration barrier for diffusion and n is the the exponent in the pre-exponential factor for diffusion. Ulbricht et al. [2002a] have used the values of E_m from molecular mechanics calculations and $n \approx 4-5$, to show that the above conditions are met for the thermal desorption of Xe from SWNT bundles.

The inhomogeneities arising from the sample surface defects and that arises due to the presence of impurities can further smear the binding energies of adsorbates and therefore result in broadening of thermal desorption peaks [Zambano et al., 2001].

2.2. Chemisorption

The chemisorption of a gas-phase adsorbate to a solid occurs when the atoms or molecules are bound to the solid surface through an overlapping of one or more of their electronic orbitals. The formation of chemisorptive bonds between an adsorbate and a solid surface requires electron transfer between them. Depending on the extent of the electron transfer, the chemisorptive bond can be predominantly ionic

or covalent. The first type is characterized by a complete charge transfer between the adsorbate and substrate while the second type is characterized by the sharing of electrons between adsorbate and surfaces.

2.2.1. Energetics of chemisorption

The energetics of an adsorbate bonded to a solid surface via chemisorption needs to be treated quantum mechanically. The basic principles of this treatment is described below.

A simple illustration of a chemisorption system is given by the adsorption of a diatomic molecule on a transition metal surface [Lüth, 2001]. For the sake of illustration, one can assume that the electronic structure of the metal is an energetically sharp, partially filled d -band. Likewise, the molecule has a partially filled molecular orbital. When the molecule approaches the metal surface, the overlap of orbitals leads to a rehybridization of surface- and molecular-orbitals and also leads to the formation of new surface-adsorbate orbitals. An approximate wave function for this adsorbate-surface system is:

$$\psi = N\psi_0 + \sum_{k < k_F} a_k \psi_{1k} + \sum_{k > k_F} b_k \psi_{2k}, \quad (2.8)$$

where ψ_0 , ψ_{1k} and ψ_{2k} corresponding to a non-bonding state (i.e., unperturbed substrate and adsorbate states), a charge-transfer state from filled metal bands into the molecular orbital, and a charge transfer to unoccupied metal Bloch states, respectively. k_F is the Fermi wave vector. The chemisorption energy levels are obtained by minimizing the energy function:

$$\hat{E} = \frac{\langle \psi | \mathcal{H} | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (2.9)$$

where \mathcal{H} is the total Hamiltonian (molecule plus substrate). For a simple two charge-transfer states, the minimized energy states are

$$E_{\pm} = \frac{H_1 + H_2}{2} \pm \sqrt{\frac{H_1^2 + H_2^2}{2} + H_{12}}. \quad (2.10)$$

Here H_1 and H_2 represent total energies of the states in which an electron is transferred from the metal to the molecule and vice versa. H_{12} is the interaction energy between the two ionic charge transfer states. For a positive H_{12} , the values E_+ and E_- are higher and lower respectively than the average ionic energy $(H_1 + H_2)/2$. These E_+ and E_- , respectively, correspond to the energies of anti-bonding and bonding orbitals formed by chemisorption. The lowering of total energy (E_-) in the bonding state favors the chemisorption. A qualitative

description of the chemisorption potential is similar to the physisorption potential (Fig. 2.2). However, the equilibrium distance, z_0 , is much smaller when compared to those of physisorption and typically has values 1–3 Å. Also, chemisorption results in stronger bonding with typical binding energies, E_b , of about an electron volt [Lüth, 2001].

In the case of molecular chemisorption, particularly diatomic molecules on transition-metal surfaces, it has frequently been observed that the rearrangement of their electronic configuration leads to the dissociation of the molecules to form new adsorbate species. A simple illustration of dissociative chemisorption is the hydrogen on a transition metal surface. The potential energy diagram corresponding to dissociative chemisorption of a neutral diatomic molecule is schematically illustrated in Fig. 2.5.

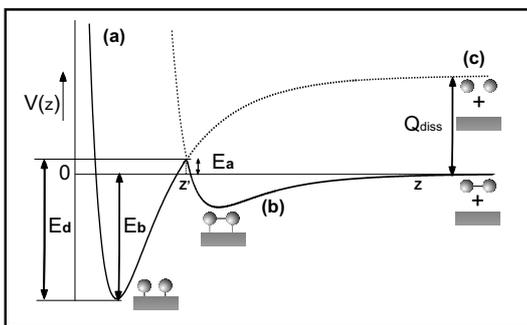


Figure 2.5.: The one-dimensional potential energy diagram corresponding to the dissociative chemisorption of a neutral diatomic molecule on a solid surface. The total potential energy curve (a) can be considered as a combination of the physisorption potential from the un-dissociated molecule (b) and the chemisorption potential of two dissociated atoms (c). The dissociative chemisorption of a diatomic molecule can be envisaged to pass through a physisorption well, known as the precursor state before bond dissociation. Q_{diss} is the dissociation energy of the diatomic molecule in the gas phase, E_b is the binding energy of chemisorbed atomic species and E_d is the activation energy of desorption. z is the distance of the molecule from the surface.

This dissociative chemisorption potential can be described qualitatively as the combination of the potential for a physisorbed molecule and the chemisorption of the corresponding atomic species. A molecule approaching the surface from a large distance, z , feels attraction to the surface, which leads to a physisorbed or precursor state. Approaching closer to the surface would cause a rapid increase in the potential energy of the system due to overlap between molecule's and substrate's electronic states. A transfer of electrons from metal to the substrate subsequently leads to a change in the molecular bond order which results in the cleavage of the diatomic molecule to form two monatomic species. These dissociated atoms can be bonded to the surface in a chemisorption state which has a much higher binding energy and a smaller equilibrium distance. The corresponding poten-

tial curve for two atoms differs from that of the molecule at the larger distance z by exactly the dissociation energy of the molecule Q_{diss} [curve (b) in Fig. 2.5]. A molecule with enough kinetic energy to overcome the activation barrier E_a will

follow the chemisorption potential: Near z' it will dissociate into two atoms, which will be chemisorbed to the surface, forming two $S-A$ (surface-adsorbate) bonds with a total adsorption energy E_b . At z' , it can be assumed that the molecular orbitals have transformed to atomic orbitals. Dissociative chemisorption is an activated process that requires a minimum kinetic energy E_a for chemisorption to occur as shown in Fig. 2.5. Since this activation barrier is lower than the gas-phase dissociation energy Q_{diss} , dissociation occurs preferentially on the solid surface. The decrease of the dissociative activation barrier by the presence of the solid surface is a feature of catalytic decomposition. From Fig. 2.5 one can also deduce that the desorption of the chemisorbed atomic species requires a minimum energy E_d , i.e., the activation energy for desorption. During desorption, the atomic species recombine near z' to form a diatomic molecule, which is detectable in the gas phase. For this process of activated adsorption the characteristic energies, E_b , E_d and E_a , are related to one another by:

$$E_d = E_b + E_a. \quad (2.11)$$

The activation energy for desorption E_d (for both physisorption and chemisorption) is experimentally obtained from a thermal desorption experiment using the Arrhenius expression as the rate of desorption [Eq. (2.4)]. One experimental distinction between physisorption and chemisorption is that in the chemisorption, one deals entirely with sub-monolayer adsorption. This is because, in chemisorption the activation energy for adsorption E_a for the first monolayer is much greater than that for the succeeding layers.

2.2.2. Chemisorption in heterogeneous catalysis

The topics of chemisorption and heterogeneous catalysis are closely intertwined. The molecular emphasis of chemisorption has benefited the field of heterogeneous catalysis by giving depth and scope to understanding the surface chemistry of catalytic processes.

Elementary steps in heterogeneous catalysis involves a sequence of events in which the chemisorption of the reactants is one of them [Laidler, 1987]. This sequence is: (1) diffusion of reactants to the surface (usually considered to be a fast process); (2) adsorption of the reactants (slow if activated); (3) surface diffusion of the reactants to active sites; (4) reaction of the adsorbed species (often rate-determining); (5) desorption of the products (often slow) and (6) diffusion of the products away from the surface (Fig. 2.6). The reaction mechanism between two adsorbed molecules on a surface was first proposed by Langmuir and Hinshelwood [Hinshelwood, 1940]. Their treatment involves obtaining an expression for the concentrations of surface reactants, and then expressing the rate of product formation in terms of these surface concentrations. In the Langmuir-Hinshelwood mechanism, the surface reaction

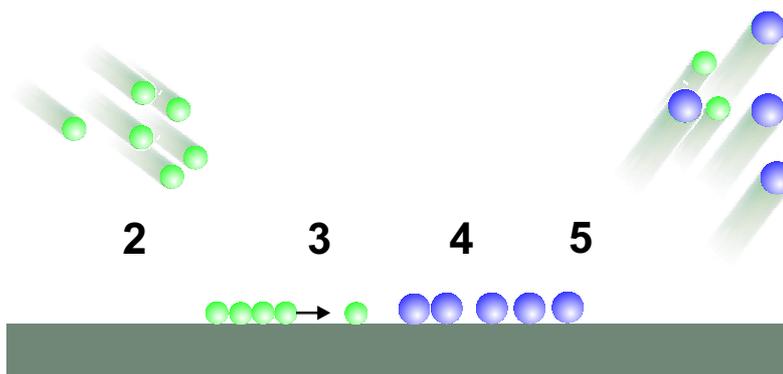


Figure 2.6.: Schematic illustration of elementary process in heterogeneous catalysis. Steps 1 and 6 (diffusion to and from the surface) are not depicted. Step 2: the adsorption of the reactants to the solid surface. Step 3: the activation of the molecules by diffusion to activated surface sites. The reaction between adsorbates (step 4) results in the formation of the products. Step 5: the desorption of the products from the surface.

and the subsequent desorption of gaseous products are considered to be a single step [Laidler, 1987]. This is considered so, because the rate of desorption is unknown in usual surface chemical reactions. The Langmuir-Hinshelwood mechanism also assumes a preserved adsorption-desorption equilibrium throughout the course of surface reaction [Campbell, 1988]. Another type of mechanism for the surface reaction is based on the reaction of an adsorbed molecule with a gas-phase molecule. This mechanism is known as Langmuir-Rideal mechanism and occurs less commonly compared to the Langmuir-Hinshelwood mechanism [Laidler, 1987].

The surface reaction between adsorbed ethylbenzene and oxygen species, known as oxidative dehydrogenation, is presented in this thesis (chapter 6) and is addressed by the Langmuir-Hinshelwood mechanism. The specific details of the mechanism pertinent to the oxidative dehydrogenation is provided in chapter 6.

