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Surface-structure dependencies in catalytic reactions

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Chapter 1

Introduction

1.1 Catalysis

The definition of a catalyst is described in the Oxford Dictionaries as ‘a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change’. Figure 1.1 illustrates the principle of a catalytic reaction. The reactants bind to the catalyst material, the molecules react and form a product, the product separates from the catalyst, and the catalyst can be used again for a new reaction. In principle, a reaction can take place without a catalyst if sufficient energy is present to overcome the high activation barrier. The catalyst provides an alternative route with lower barriers.

Catalysts play a very important role in life, industry, and the environment. There are three different main types of catalysis, namely: biological, homogeneous, and heterogeneous catalysis. Enzymes are very specific and efficient catalysts and they play a crucial role in all biological processes. An example of a biological catalyst is yeast. It has been used for centuries to make alcoholic drinks. In homogeneous catalysis, both the catalyst and the reactants are in the same phase, usually the gaseous or liquid phase. The advantage is that all catalyst particles can participate in the reaction. A disadvantage is that it is difficult to recover the catalyst materials from the reaction mixture. Heterogeneous catalysis is the most common type of catalysis used in industry for the production of fine chemicals and materials. A heterogeneous catalyst is in a different phase than the reactants. The catalyst is usually a solid material, while the reactants are gases or liquids. Only the catalyst

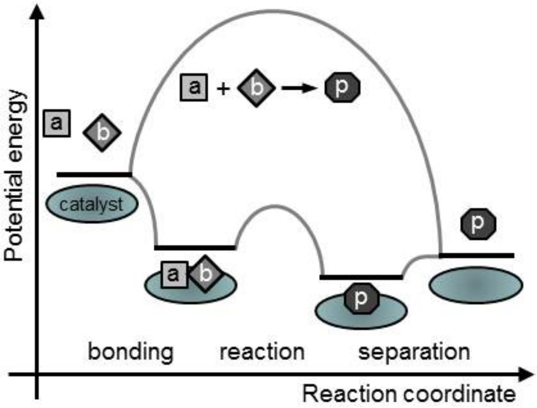

Figure 1.1: Potential energy diagram of a heterogeneously catalyzed reaction. Adapted from[1].

material near the surface participates in the reaction. It is easier to separate a solid catalyst from the reaction mixtures than in homogeneous catalysis. The research in this work involves heterogeneous catalysis.

1.2 Heterogeneous catalysis

Precious metals, such as platinum and palladium, are good catalytic materials for various reactions. In heterogeneous catalysis, only the surface of the solid participates in the reactions. Therefore, it is important that small particles with a large surface area, named nanoparticles, are used. The surface atoms have a different structure than the bulk atoms. Surface atoms have fewer neighboring atoms and can interact with reactants. A typical reaction cycle in heterogeneous catalysis includes adsorption of reactants on the surface, a reaction, and finally desorption of the product(s). For this process, it is important that the reactants and products bind strong enough to the surface, so that the reaction can take place. At the same time the molecules should not bind too strongly to the surface to prevent molecules from blocking the active sites and kill the catalytic activity.

Molecules can adsorb to the surface in three ways. The first type of adsorption is physisorption. The molecules have a very weak van der Waals interaction with the surface. The chemical identity of the surface and the adsorbates are still intact.

The second type is molecular chemisorption. The molecules adsorb and form a new bond with the surface, while the molecular bonds stay intact. The last type of adsorption is the dissociative chemisorption. The bonds in the molecule are broken, different segments have now formed new bonds with the surface. The adsorbed species can form new compounds, which will then desorb from the surface.

1.2.1 Three-way catalytic converter

The most well known example of a catalyst is likely the one in our car exhaust: the three-way catalytic converter. It converts harmful gases into benign products.

$$2CO + O_2 \rightleftharpoons 2CO_2 \tag{1.1}$$

$$4C_xH_y + (4x + y)O_2 \rightleftharpoons (4x)CO_2 + (2y)H_2O \tag{1.2}$$

$$2NO + 2CO \rightleftharpoons N_2 + 2CO_2 \tag{1.3}$$

The most efficient catalysts for the oxidation reactions (1.1 and 1.2) are platinum and palladium. For the nitric oxide reduction reaction (1.3), rhodium and palladium are the most efficient. Platinum and rhodium are used most often in the three-way catalytic converter, but palladium can replace both precious metals. For an optimal conversion of all gases, a proper air-to-fuel ratio and operating temperature are necessary[1].

1.2.2 The fuel cell

The proton exchange membrane fuel cell (PEMFC) is a promising hydrogen fuel cell for applications in transportation and mobile electronics[2]. A schematic overview of a PEMFC is shown in figure 1.2 (adapted from[3]). The hydrogen oxidation reaction (HOR, reaction 1.4) takes place at the anode and the oxygen reduction reaction (ORR, reaction 1.5) at the cathode. In the overall reaction (reaction 1.6), hydrogen and oxygen are converted into water and energy.

$$2H_2 \rightleftharpoons 4H^+ + 4e^- \tag{1.4}$$

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \tag{1.5}$$

$$2H_2 + O_2 \rightleftharpoons 2H_2O + \text{energy} \tag{1.6}$$

Platinum is one of the metals that is sufficiently active to activate O_2, and at the same time noble enough to release oxygen in the form of water from the surface. Yet, a suitable catalyst should show at least two to four times more stable catalytic activity than Pt alone[4]. A possible solution is the use of bimetallic catalyst materials, such as Pt_3Sc or Pt_3Y[5].

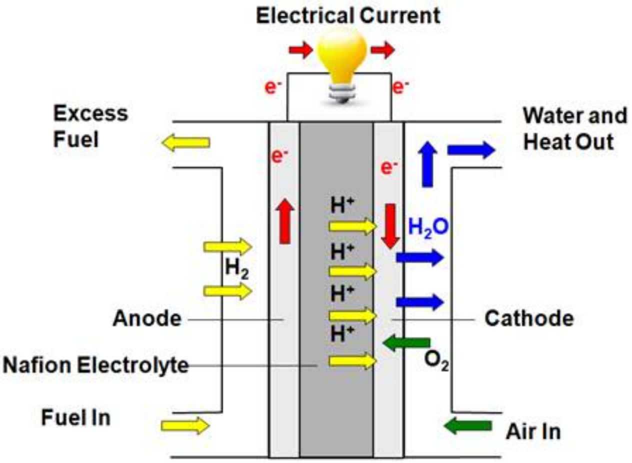

Figure 1.2: Schematic overview of a proton exchange membrane fuel cell (PEMFC), adapted from[3].

1.3 Surface science

Heterogeneous catalysts are widely used and often very expensive (e.g. PtNi and PtFe). It is important to improve our understanding of the interaction of the reactants and products with the catalytic surface in order to obtain better and cheaper catalyst materials for the future. Theoretical studies can provide fundamental insights in the processes and mechanisms taking place on the surface. They can help in predicting new and promising catalysts[6]. The state-of-the-art methods and techniques now make it possible to reach chemical accuracy[7]. Nevertheless, it is still difficult and expensive to include all possible interactions, defect sites, and larger molecules. Electrochemical catalytic studies are closer to reality than many gas-phase studies. Measurements are performed in an aqueous environment and effects of, e.g. pH and potential can be studied. However, the electrolyte itself makes it difficult to probe the solid-liquid interface. Ultra-high vacuum (UHV) studies may form a bridge between theory and electrochemistry.

1.3.1 Ultra-high vacuum

In an ultra-high vacuum chamber, the pressure is usually lower than $1 \cdot 10^{-9}$ mbar. The reaction conditions can be controlled quite accurately. Depending on the pressure and type of molecules in the chamber, the catalytic surface remains clean for a relatively long time. The amount of adsorbate and its energy can be controlled by leaking in different amounts of gas or by using a (supersonic) molecular beam. Various UHV techniques, e.g. temperature programmed desorption (TPD), low energy electron diffraction (LEED), and the King and Wells (KW) technique[8], can be used to obtain insight on the fundamental processes that take place at surfaces during reaction, e.g. adsorption, reaction, desorption. These techniques are explained in more detail in chapter 2.

One of the major draw-backs of using UHV, is the large difference in pressure between catalysis in UHV and industry. In UHV, the pressure is more than 12 orders of magnitude lower. This is also known as the pressure gap. Nowadays, various techniques are developed to study the interaction between the reactants and catalytic surface under more realistic pressures. Nevertheless, a combination of all different types of studies is necessary to understand the reaction mechanisms and processes in the most complete way.

1.3.2 Surfaces

The surface science approach has a second draw-back: the materials gap. Real nanoparticles have a large variation in surface orientations. Small particles have a relatively large number of steps and kinks (defect sites) compared to larger particles. Interpreting results from real nanoparticles is very difficult because of the large variation in facets. Therefore, well-ordered single crystal surfaces are often used in surface science. Flat surfaces such as Pt(111) (hexagonal surface structure, figure 1.3a), Pt(100) (square structure, 1.3b), and Pt(110) (rectangular structure, 1.3c) have been studied extensively. However, defect sites are thought to be more active in bond breaking and making reactions[9]. To study the influence of steps on the reaction, stepped (see chapter 5 and 6) or curved single crystals can be used.

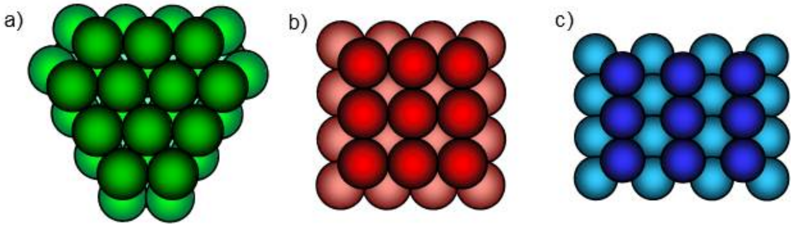

Figure 1.3: Schematic view of the a) (111) (hexagonal atomic arrangement), b) (100) (square), and c) (110) (rectangular) surface structures.

1.4 Scope of this thesis

The focus of this thesis is on the dissociation of O_2 on Pd and Pt and the hydrophobic/hydrophylic interaction of water with deuterium-precovered Pt. The breaking of the oxygen-oxygen bond is an important step for various reactions, such as the CO oxidation in the three-way catalytic converter and the catalytic oxygen reduction in the PEMFC. Most real catalytic processes involve more than one reactant that is in contact with the catalytic surface. In the PEMFC, water, hydrogen, and oxygen are present. Therefore, it is interesting to study the interaction between water, deuterium, and the surface. We use single crystal surfaces and supersonic molecular beam and UHV techniques to improve our knowledge on these systems.

In chapters 3 and 4, oxygen dissociation on the flat Pd(100) crystal as a function of incident energy (E_i), surface temperature (T_s), and incident angle is studied. The focus of chapter 3 is on the initial sticking probability of oxygen on Pd(100). The results are compared to Pd(111) and Pd(110). The results provide insight on the dissociation mechanism in the zero-coverage limit. In chapter 4, the sticking of oxygen on Pd(100) as function of coverage and oxygen desorption in the subsequent TPD experiments are studied. The dissociation process changes with increasing oxygen coverage. The obtained maximum oxygen coverage depends on both surface temperature and incident energy.

Oxygen dissociation as function of E_i, T_s, and angle is also studied on the stepped Pt(553) single crystal (chapter 5). We compare our data to the flat Pt(111) and stepped Pt(533) surfaces to study the influence of step sites. Pt(553) and Pt(533) have a comparable terrace width, but a different step type. The presence of step edges leads to a higher reactivity than on the flat surface. Depending on kinetic energy, the step type also plays a role in the oxygen sticking and dissociation processes.

In chapter 6, co-adsorption of water and deuterium on stepped Pt surfaces with the (100) step type is studied. Earlier studies showed that the deuterated Pt(533) surface is hydrophobic, while D/Pt(111) and D/Pt(553) are hydrophilic. It was expected that a larger terrace separated by (100) steps might reduce the hydrophobicity. We compare the Pt(533) surface to Pt(755), Pt(977), and Pt(111) and find that even 8-atom wide terraces do not resemble the 'ideal' (111) surface.

Chapter 7 provides an outlook on future experiments and proof-of-principle for double molecular beam experiments. We show that reactions can take place on stepped surfaces when one gas is provided by the supersonic molecular beam and the other by the effusive beam. We can form HD from H_2 and D_2 on Pt(553) and HOD from O_2 and a mixture of H_2 and D_2 on Pt(533). The effect of step type and step density will be studied on curved single crystals in the future.