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Chapter 1

Introduction

1.1 Heterogeneous catalysis

The phrase catalysis was coined by Jöns Jakob Berzelius who in 1836 was the first to describe reactions that are accelerated by substances that remain unchanged after the reaction[1]. Catalysis plays an important role in biology and chemistry. It modifies the kinetics for the reaction, modifies the pathway of the reaction and steers a reaction toward a specific product.

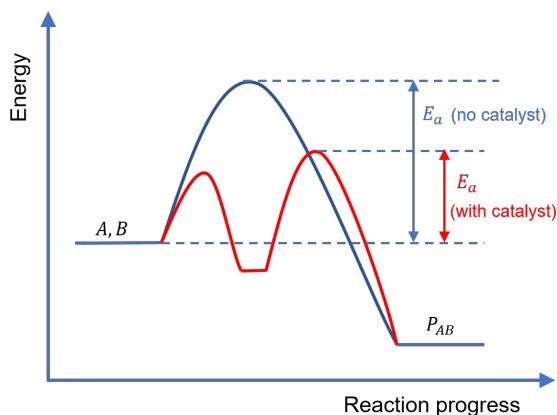


Figure 1.1: Generic potential energy diagram showing the effect of a catalyst in a hypothetical exoergic chemical reaction $A + B \rightarrow P_{AB}$. The presence of the catalyst opens a different reaction pathway with a lower activation energy.

There are three types of catalysis. Biocatalysis, where the catalyst is an enzyme. Homogeneous catalysis, where the catalyst is in the

same phase as the reactant and product. Heterogeneous catalysis, where the catalyst is in a separate phase. The obvious advantage of heterogeneous catalysis is the easy separation of product and catalyst. Heterogeneous catalysis is widely used in industrial catalytic processes like the Sabatier reaction for synthesizing methane from CO_2 , the car exhaust gas system[2] and fuel cells[3]. This thesis describes studies into elementary steps in heterogeneous catalysis.

In a heterogeneously catalyzed reaction, the following steps occur: diffusion of reactant to the catalyst, adsorption and diffusion of reactant on the surface of the catalyst, reactions on the catalyst surface, desorption of product from the catalyst surface and diffusion of product away from the catalyst. The understanding of the mechanism of reactions, notably the adsorption step on the catalyst surface, is the goal of research. Here, we investigate how elementary steps depend on the structure of the surface.

For a real catalyst, the structure and surface is not homogeneous. The reactions are not taking place at the entire surface but have favorite active sites. The fundamental understanding of the active sites and the reaction mechanism can help us improve the design and synthesis of new catalysts. But it is difficult to carry out such research for a real catalyst, working under industrial conditions.

To simplify the question, working under vacuum, using well characterized single crystalline surfaces and simple reactions has proven to be a good approach.

1.2 Ultra-high vacuum

Vacuum is a space devoid of matter. A perfect vacuum is ideal and not achievable in reality. An approximate of a perfect vacuum is a region that the residual gas pressure is so low that it takes on the order of an hour to cover a surface with one monolayer of residual gas molecules.

Ultrahigh vacuum (UHV) always refer to a pressure less than 1×10^{-9} mbar. The UHV condition can be obtained by using specially designed vacuum pumps, such as a series of a rotary pump, turbo pump and/or an ion pump. UHV conditions are an integral ingredient for science research. Surface science experiments always need a chemically clean surface without any unwanted adsorbates, which under UHV remains clean for a longer time, say, 10 minutes. Most surface analysis

techniques, such as low energy electron diffraction (LEED), require at least high vacuum conditions for the transmission of an electron beam.

In a properly designed UHV system, several surface science experiments can be carried out. By using an Ar sputter gun the surface can be cleaned. Many surface analysis tools can be used to study the surface, like a scanning tunneling microscope (STM), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The reactant, always in the gas phase, is introduced into the UHV chamber by using a leak valve or by using a molecular beam. The reaction conditions, such as temperature and pressure, can be controlled. The product can be detected in the gas phase by using a quadrupole mass spectrometer (QMS).

1.3 Simple surface

The surface of a real catalyst is very complex. It may contain steps, kinks and facets etc. It is difficult to identify the active sites. By using a well-defined single crystal surface, we have control over which types of sites are provided. We can study the effect of various types of sites using different single crystal surfaces.

The use of the single crystal surface also has disadvantages. To fully understand the reaction mechanism of reactions on real complex catalyst surfaces, several single crystals with different crystal faces are needed. This is expensive and repeating experiments on various crystal surfaces takes a lot of work and time. If we can introduce different structures onto one single crystal in some order and measure the reactivity locally, then we can study the catalytic reactivity simpler and faster. Chapters 5 and 6 in this thesis show the use of a curved Pt(111) surface to study the step density dependence of HD formation and O₂ sticking on Pt surface.

1.4 Simple reaction

We always use small molecules in this thesis, such as H₂, D₂ and O₂ etc. The dissociative adsorption of a diatomic molecule on a surface follows a series of steps, the first of which on the surface is:



which is the simplest initial step for heterogeneous catalysis. The reverse reaction is the recombination and desorption of a diatomic molecule from surface.

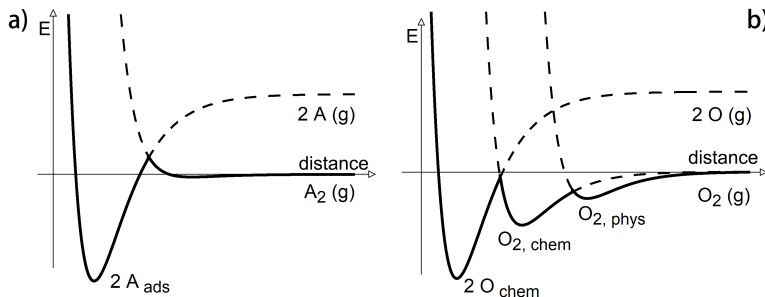
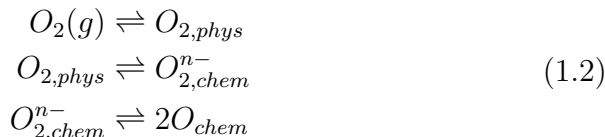


Figure 1.2: a) shows the energy diagram for dissociative adsorption of diatomic molecule, as equation (1.1) describes. b) illustrates hypothetical one dimension potential energy surface for equation (1.2).

For complex reactions containing intermediate states, like O_2 on Pt surface:



the dissociative adsorption may occur via physisorption and chemisorption states. Figure 1.2 illustrates the one-dimensional potential energy surfaces of equation (1.1) and (1.2).

One advantage of using small molecules is that these are relatively easy to model by theory. Then the experimental and theoretical results can be combined to obtain a deeper understanding of the mechanism. Calculations are usually separated into two parts. The Born-Oppenheimer approximation is used assuming that the energy of the electronic system of the reactants and the surface can be calculated for fixed positions of the nuclei. This gives a potential energy surface (PES) for the interacting particles. The dimensions of the potential energy surface for a small molecule with a surface are not too large to calculate using Density Functional Theory (DFT). The PES allows to calculate the molecular and surface motion using classical mechanics or quantum mechanics. Figure 1.3 shows a coordinate system of a diatomic molecule with a fcc (111) surface. The motion of the molecular center of mass is represented by the set of coordinates (X, Y, Z) , the orientation of the molecular axis is represented by the angles $(\theta$ and

ϕ), the stretching of the molecule is represented by coordinate r . The surface atom motion, which also could take into account, is not shown in this figure. The figure also shows some low coordinate sites such as steps, kinks, corners etc.

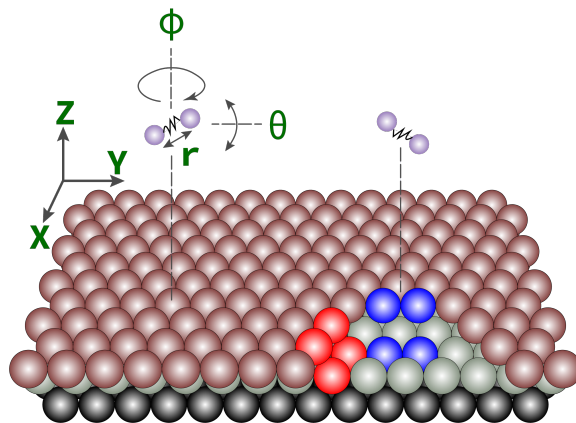


Figure 1.3: Coordinate system of diatomic molecule with a fcc-(111) surface. The surface also contains defects. The red and blue atoms indicate the (100) (also called A-type) and (110) (B-type) step, respectively.

1.5 Reactions on surfaces

For the simplest reaction on surface in which a bond is broken, i.e. dissociative adsorption of a diatomic molecule, there are two mechanisms. First is the direct mechanism. In this case, a molecule incident from the gas phase directly dissociates upon the collision with surface. This process may be activated depending on the type of molecule and surface. The other mechanism is the trapping-mediated mechanism. The molecule is trapped on the surface in a weak physisorption or chemisorption state. It diffuses on the surface until it finds an active site where it can dissociate. As the interaction between the molecule and the surface is weak, the molecule has a finite residence time on the surface. Subsequently it may desorb or dissociation.

Reactions on surfaces can take place through several mechanisms. The most common is the Langmuir-Hinshelwood (LH) mechanism[4, 5]. In this mechanism, the reactants are trapped or dissociated on the surface. Two or more adsorbed species meet through thermal diffusion and react on the surface. Then the product desorbs from the surface.

Another mechanism is the Eley-Rideal (ER) mechanism[6, 7]. In this mechanism, one reactant is on the surface, the other collides with it directly from the gas phase without equilibration or diffusion. The the reaction takes place upon the collision, followed by a desorption of product. An intermediate mechanism is the hot-atom (HA) or Harris-Kasemo mechanism[8]. It is in between the LH and ER mechanism. In this mechanism, one reactant coming from the gas phase, bounces around on the surface for a short period of time, and then reacts with another reactant adsorbed on the surface without having thermalized. Another mechanism, that is introduced by Mars and van Krevelen[9] is not relevant to this thesis.

1.6 Scope of this thesis

The research presented in this thesis makes use of small molecules (as H_2 , D_2 and O_2) on well-defined single crystal surfaces (flat Pt(111), flat Cu(211) and curved Pt(111)) to elucidate the role of surface structure and degrees of freedom in the reactant in specific surface reactions.

In chapter 2, we briefly describe the experimental apparatus and the general experimental techniques used in this thesis.

In chapter 3, we investigate geometric corrugation for D_2 dissociation on Pt(111) by mapping the dependence of the initial reaction probability on incident kinetic energy and polar angle for two different azimuths. In accordance with predictions from dynamical calculations of dissociation on an SRP-based potential energy surface, we find at most a very weak signature of geometric corrugation at large polar angles.

In chapter 4, we present a combined experimental-theoretical study on structural and coverages dependences of the adsorption and desorption of molecular hydrogen on atomically flat Cu(111) and highly stepped Cu(211) surfaces. For molecules with identical incident energy from supersonic molecular beams, we find a reduced dissociative sticking probability for the stepped surface compared to Cu(111). DFT calculations of activation barriers to dissociation for the clean and partially precovered surfaces, as well as quantitative analysis of TPD spectra support that the A-type step of the (211) surface causes an upward shift in activation barriers to dissociation and a lowering of the desorption barrier. The new data allow us to determine low stick-

ing probabilities at conditions where King and Wells measurements fail to determine the reactivity. They are also fully consistent with the unexpected observation that monoatomic steps on a surface lower the reactivity toward the dissociation of a diatomic molecule.

In chapter 5, we introduce (100) and (110) steps at varying step density onto a surface consisting otherwise of (111) planes by using a curved Pt(111) single crystal. As HD formation from H_2 and D_2 incident onto Pt at low incident energy is very sensitive to the step density, we use an anti-seeded supersonic molecular beam to probe surface structure variation along on the curved surface. HD formation increases linearly from the (111) apex of the crystal to the edges when the curved crystal is cleaned and annealed at 850 K. It reflects the dominance of the indirect dissociation mechanism of molecular hydrogen occurring at step sites and the linear step density variation with position on the crystal. A LEED study confirms the structural variation through a spot-splitting analysis. When the curved crystal is cleaned using the same procedure but annealing occurs at 1200 K, HD formation is non-linear. Reactivity is strongly reduced over the entire A-type step side of the crystal. Here, the surface seems to restructure by formation of large (100) facets. For the B-type step side, steps remain monoatomic except near the (443) plane. It shows that, in contrary to common belief, it is the 7-atom wide (111) terrace with B-type steps that is unstable and not the 8-atom wide (997) surface. Although changes are observable in LEED patterns, our study shows that H-D exchange as a chemical probe is much more sensitive to surface structure changes caused by higher annealing temperature.

In chapter 6, we present the first study combining curved single crystals and stereodynamical control of impinging O_2 to unravel how monoatomic steps improve oxidation kinetics. Based on general principles, defect sites on Pt catalyst particles may be expected to enhance reactivity, but the reaction dynamics underlying such improved kinetics remain largely unexplored. Our results show that at low incident energy, steps dominate reactivity by providing means for an indirect dynamical trapping mechanism with no orientational dependence to the incident O_2 molecule. At higher impact energy, a direct chemisorption mechanism dominates. For the step facet, we show that it favors molecules impacting with their internuclear axis parallel to its surface. Combined with the contribution of atomically flat terraces, stereodynamical filtering controls reactivity at high temperature conditions.

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