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1 Introduction

1.1 History of Catalysis

Catalysis had been applied by humans long before the concept of catalysis was described for the first time:

Probably one of the oldest uses of applied catalysis is the biocatalytic (enzymatic) process of fermentation in food production. Food can be made more tasty and longer lasting this way. My favourite examples are salami, yoghurt, coffee and cacao. Probably even better known products are wine and beer.

An example for the early industrial application of catalysis is the lead chamber process for the production of sulphuric acid. In this process $\text{SO}_2$ is oxidized to $\text{SO}_3$ by NO, delivering a fairly diluted product [1,2]. It had been known since the Middle Ages. It was employed industrially in England in the middle of the 18$^{th}$ century. An early patent in the area of catalysis stems from 1831 and as well describes a way of producing sulphuric acid by a finely divided Pt catalyst [1,3]. That patent was turned into use for the production of fuming sulphuric acid by Messel in 1875 [1].

All-day life applications in the mid 1800s are the Döbener lighter and Davy’s miner’s safety lamp. In Döbeners lighter hydrogen was produced when zinc came in contact with diluted sulphuric acid. The hydrogen flowed over spongy platinum and reacted with oxygen from the air igniting into a small flame [4]. Davy introduced his miner safety lamp in the Philosophical Transactions of the Royal Society [5]. He embodied a fine sheet or fine coils of platinum wire on top of a flame into a wire-gauze cylinder. The fine wire cage allowed for gas (especially firedamp (explosive
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gas mixture in mines)) to move into the cylinder but the flames could not propagate through it. The fine mesh of metal cooled the gas coming out of the lamp to ambient temperature, thus substantially decreasing the risk of explosions. Another effect was that the intensity of the flame gave an indication on the amount of firedamp present. If the amount of explosive gas was too high, the flame extinguished but the Pt wire remained glowing intense enough to provide the miners with light.

Nowadays catalysis is even important for our everyday lives, although we are generally not aware of it. Fuels, polymers and monomers for plastics (like PET, for example) would be much harder to obtain without catalysis. Imagining a life without those products would be difficult, especially for younger generations. No plastic packings in supermarkets; no plastics in the living room (thinking of mine: that would be quite bare and uncomfortable); very different ways of personal mobility.

Although the inventions of those products and their production all play a role in environmental pollution and the use of non-regenerative resources, the same science that created the problems, I believe, will be able to solve them: Catalysis.

An example of that is the three way catalyst of a car. It reduces the amounts of pollutant from car exhaust significantly. It oxidises CO and hydrocarbons to CO$_2$, or CO$_2$ and water, respectively. NO also reacts with CO to from CO$_2$ and N$_2$. These products are less damaging to the environment than the initial combustion products of the engine. Nevertheless, the massive production of CO$_2$ caused by the sum of all traffic remains a problem.

Having pointed out the importance of catalysis, it is not surprising that chemistry students learn definitions for terms like ‘catalyst’ in their first year:

A catalyst is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself in the process [6].

More or less the same words can be found in almost any basic chemistry textbook. Commonly this is accompanied by a statement that the reaction energy and equilibrium of a reaction are not influenced by a catalyst [7].

Though research has made substantial progress since the creation of the terms ‘catalyst’ and ‘catalytic force’ were formed by Berzelius in 1836 [8], still many even
1.2 General Principles of Catalysis

As already stated in the previous section, the position of the equilibrium and the
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absolute energetics of a reaction are not influenced by the catalyst. The only effect of a catalyst is a lowering of the activation barrier(s) leading to faster equilibration. This is depicted schematically in figure 1.1. It shows an energy diagram for a model reaction \( A + BC \rightleftharpoons AB + C \). The catalysed pathway is shown in black while the non-catalysed reaction in shown in grey.

Another important aspect in catalysis is the selectivity of catalysts. Catalysts can for example kinetically favour the production of a thermodynamically unfavourable product and therefore allow for the production of this compound. If the reaction would not be stopped at a time favourable for that product, ultimately the thermodynamic equilibrium would be reached.

Depending on the type of catalyst there are different types of interaction that lead to the same goal.

While homogenous catalysts in many cases tend to catalyse specific reaction with a multitude of reactants, biocatalysts like enzymes are generally more specific. Many enzymes only accept certain compounds for reaction and are even able to discriminate between different stereo isomers.

Heterogeneous catalysts are generally metal and/or metal oxide particles supported on other materials and ease the bondbreaking of otherwise rather stable molecules, frequently leading to adsorption onto the surface. There the so activated species can further react.

1.2.1 Homogeneous Catalysis

Well known examples for homogeneously catalysed processes are the Pd-catalysed Heck-, Negishi, and Suzuki reactions. For the development of these reactions Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki were awarded the Nobel prize in chemistry 2010.

The reactions developed by the three chemists have in common that all are Pd-catalyzed cross-coupling reactions. The general processes occuring in all three types of reactions are similar, but there are some differences to the Heck-reaction shown in figure 1.2: In a Suzuki reaction bor-organyles are used instead of vinylic
compounds (methyl acrylate in this example). In Negishi reactions zink-organyles are employed. Instead of the insertion a transmetallation occurs in both cases. The product is then formed in a reductive elimination yielding the restored catalyst without further reaction steps.

In the speech during the award ceremony Professor Jan-Erling Bäckvall said [10]: ‘The palladium-catalysed cross-couplings have been used for large-scale industrial manufacturing of, for example, pharmaceuticals, agricultural chemicals, and organic compounds that are used by the electronic industry,’ pointing out that way the importance of their developments for today’s society.

A remarkable aspect of not only the Heck-reaction but many catalytic processes in homogeneous media is the fact that the steps of the catalytic cycle are known. For most biocatalytic and heterogeneously catalysed processes this is not the case. One of the very rare exceptions in heterogeneous catalysis is the catalytic ammonia production.

### 1.2.2 Biocatalysis

Biocatalysis is done by enzymes. Compared to many cases of homogeneous catalysis reaction conditions are rather mild as the enzymes would otherwise denature and become ineffective. Some enzymes are specialized in catalysing one specific reaction and will accept multiple substrates while others are highly specialized and can even discriminate different stereoisomers by reacting with only one of them. This is often referred to as a ‘lock and key’ mechanism as depicted in figure 1.3.

There are almost uncountable examples for biocatalytic processes. We only have to look within our own bodies or all living things around us.

One of the probably most important examples is the production and utilization of the body’s energy carrier ATP (adenosine triphosphate). In 1997 the Nobel Prize in Chemistry was awarded half to Paul D. Boyer and John E. Walker for the elucidation of the enzymatic process producing ATP and half to Jens C. Soku for the
Figure 1.2: Heck reaction cycle. Iodobenzene is coupled with methyl acrylate to form trans-methyl cinnamate. A) oxidative addition of Iodobenzene, B) coordination of methyl acrylate, C) insertion of methyl acrylate into Pd-benzyl-bond, D) β-H elimination of product, E) dissociation of product from complex, F) reductive elimination of side-product. The reaction was chosen from a paper by Heck [9] and displayed according to the reaction steps he proposed.
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Figure 1.3: Schematic of an enzyme catalyzed reaction.

first discovery of an ion transporting enzyme (Na$^+$, K$^+$-ATPase). Both processes are absolutely fundamental for organisms from single cells to complex life.

1.2.3 Heterogeneous Catalysis

In heterogeneous catalysis the catalyst and reactant are not in the same phase. That means reactions take place at interfaces. This applies to many large scale processes in chemical industry. One famous example known to every chemistry student is the Haber-Bosch process. Fritz Haber and Carl Bosch, received Nobel prizes for their contributions to the ammonia synthesis in 1919 and 1931, respectively.

The Haber-Bosch cycle provides a very fruitful example of this type of catalysis. In this reaction nitrogen and hydrogen are forming ammonia which is a basic product for the chemical industry. In 2011 about 131 million tons of ammonia were produced world-wide [11].

\[
N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H_{298}^0 = -46.1kJ/mol
\] (1.1)

Although the synthesis of ammonia appears to be a simple example, the number
of reaction steps necessary is 7 in the most straightforward model [12] which is excluding the possibility of the formation of (unstable) side products. This model is given by equations 1.2 a-g. The star represents free adsorption sites at the catalyst surface. The existence of those sites is essential. Without them no catalytic process can occur at any surface.

\[
\begin{align*}
H_2(g) + 2* &\rightleftharpoons 2H(ads) \\
N_2(g) + * &\rightleftharpoons N_2(ads) \\
N_2(ads) + * &\rightleftharpoons 2N(ads) \\
N(ads) + H(ads) &\rightleftharpoons NH(ads) + * \\
NH(ads) + H(ads) &\rightleftharpoons NH_2(ads) + * \\
NH_2(ads) + H(ads) &\rightleftharpoons NH_3(ads) + * \\
NH_3(ads) &\rightleftharpoons NH_3(g) + *
\end{align*}
\]

Industrially, the Haber-Bosch process requires high pressures (>200 bar), high temperatures (>670 K), and an Fe/K/CaO/Al_2O_3 catalyst is used. Although the iron catalyses the reaction the other compounds fulfil beneficial roles for the performance of the catalyst. The aluminium oxide hinders the sintering of the reactive iron clusters. It is a structural promoter. Supposedly the CaO plays a similar role. Potassium on the other hands acts a an electronic promoter, preferentially segregating to the surface of the Fe clusters [12]. The iron clusters preferentially expose a (111) facet [13].

This preference of iron to make a certain surface available leads to the question whether the surface structure of the iron patches is important for the reactivity. Therefore, Ertl et al. studied the dissociation of nitrogen on Fe(100), Fe(111), and Fe(110) [14, 15]. Their results indicated that Fe(111) is indeed the most active surface as N_2 dissociated with an initial adsorption energy of \(\sim 0\) kJ/mol [14,15]. This result might be considered surprising considering the bond strength of 941 kJ/mol for the N_2 triple bond. The iron in the catalyst can counteract that by formation of an iron-nitrogen bond. The strength of this bond matches perfectly with the needs for the desired reaction: N is bound strong enough to the surface that recombination and desorption do not diminish reactivity towards ammonia, and at
the same time not too strong as that would hamper reactivity, too. For his thorough research covering the fundamental science of the Haber-Bosch process and other fundamental processes Ertl was awarded a Nobel Prize in 2007.

### 1.3 Research Discussed in This Thesis

The title of this thesis ‘step away from flat land’ is a reference to several aspects of this research. The first one is the surface structure of the studied surfaces. The second one is more general and treats my personal concern with model catalysts. You have to have a reasonably “simple” system for principal investigations but the simplicity can leave you with problems when translating your results to “real live” catalysts. Unfortunately I can not claim that stepped surfaces and especially the cylindrical sample resolve those issues completely as the research presented here is still far away from industrial conditions. Nevertheless I think that increasing the complexity of the system pushes the limits of our understanding. My hope is that a detailed understanding of catalytic processes at the molecular level will help to develop more efficient catalysts and/or new technologies for a more sustainable future.

The research presented in this thesis makes use of model catalysts - single crystals of platinum and nickel - to elucidate the role of surface structure in specific surface reactions. The main focus lies on studying the very basic reaction in equation 1.2 a by means of supersonic molecular beam techniques.

After more detailed information about the set-up and general experimental techniques, the concept of single crystals will be introduced and discussed with the example of hydrogen dissociation CO precovered Pt(533) (see Chapter 3). It will be shown how CO acts as a poison on this model catalyst and significantly hampers hydrogen dissociation.

Then the concept behind the cylindrical Ni single crystal will be explained in the following chapter. Emphasis will be on how experiments are performed practically and what important modifications (regarding set-up and procedures) compared to the use of ‘flat’ single crystals had to be done (Chapter 4).

A chapter dedicated to structure determination (Chapter 5) on the cylindrical
single crystal will show to resolve specific experimental issues arising from this experimental constellation.

Successively a detailed study of deuterium dissociation on the cylindrical Ni sample will be presented (Chapter 6). In this chapter the influence of step density will be demonstrated in unprecedented detail. Further the kinetic energy dependence of deuterium dissociation will be determined for a wide range of surfaces with different surface morphologies.

Bibliography


