

Chapter 1

Introduction

Thinking about how different our world is now compared with how it was just a hundred years ago would lead any of us to wonder. But if we were asked about the most relevant changes during that time or about the most important inventions or developments of the past century, almost none of us would think of heterogeneous catalytic processes. However, a heterogeneous catalytic process can be considered as the main factor of one of the biggest changes in human world in the last hundred years: The huge increase of population. A population which grew from around one and a half billion people in 1900 to today's six billion (approximately).

For a hundred centuries the staple food of most people had been the agricultural crops which supply the human race with almost nine-tenths of the essential amino acids to synthesise the body proteins needed for tissue growth and maintenance. Early farmers soon realised that fields never allowed to rest became impoverished and that planting legumes restored the land. Peas and lentils were sown along with cereals on the first farms of the Middle East, the New World grew beans and maize, soy and mung were planted alongside Asian rice, and peanuts aided sub-Saharan root crops. These early farmers did not know that legumes provide the soil with the necessary nitrogen in a form (bound or fixed nitrogen) which can be assimilated by the plants. With industrialisation, the burgeoning of human population and of its expectations demanded high grain production. Moreover, the products of the soil were carried off from where the crops were grown to far-off places where they were consumed (i.e. the bound nitrogen was no longer returned to the earth from which it was taken). To solve the problem, wide new lands were brought into cultivation in Russia, America and Australia, but well-off countries (like England or Germany) that had little new land, started to seek new nitrogen sources to increase their own grain yields. At that time the main fertilisers were manure from animals or people, then referred to as "night soil" by the ever-discrete English people. By 1850 a new source of usable nitrogen came into play: The soluble nitrogen-rich excreta of seabirds (*guano*) that had been piling for centuries on a few islands off the shores of Peru. However, just 20 years later, the *guano* piles were levelled: 20 millions tons were moved to fertilise fields all over the world. This number gives us an idea of the magnitude of the problem. By the end of the century the Peruvian *guano* was substituted by the deposits of *caliche*, a crude

mineral conglomerate of salts, including nitrates, which had been laid down during the Quaternary era in the Chilean desert near Peru. However, by comparing the fast-rising requirements with the calculated deposits of this material, it became clear that sooner rather than later a mayor emergency would be unavoidable.

By the middle of the 19th Century, it was already known that a supply of nitrogen was necessary for the development of food crops. In 1888 Hermann Hellriegel and Hermann Wiltfarth discovered that the nodules on legume roots behave more as an active site of enzymatic nitrogen fixation than as simple storage organs. *Rhizobium* bacteria present in legume roots fix the nitrogen by combining it with hydrogen to form ammonia (NH_3) (Nature also fixes nitrogen when, during thunderstorms, lightning combines nitrogen and oxygen in the upper layers of the atmosphere to produce nitric oxide, NO , which is carried to the ground by the rain). Plants cannot assimilate elementary nitrogen (the inert N_2 present in abundance in the atmosphere) but require the nitrogen to be fixed in order to be able to absorb it. Nature knew the way to do it, but not the human race. At least not yet. It was Sir William Crookes who declared in 1898: "It is the chemist who must come to rescue". And so it happened, although not in England, but in Germany. In those days, most of the efforts of the chemistry community were devoted to imitating Nature by combining nitrogen with oxygen (to produce nitric oxide) providing the necessary energy via electric sparking. However, these attempts were very energy demanding. In 1908 the Badische Anilin- und Soda- Fabrik (BASF) got in touch with Fritz Haber, a Professor at the Technische Hochschule in Karlsruhe who was already investigating the artificial fixation of nitrogen. As related by Haber himself in his Nobel lecture, BASF wanted him to continue his investigations "*...to obtain improved efficiency from electrical energy in the combining of nitrogen and oxygen...whereas they agreed with every caution to the proposal to back me in the high-pressure synthesis of ammonia*". One year later, Haber (who worked in collaboration with Robert le Rossignol) wrote a letter to the company's directors in which he described his success in the high-pressure synthesis of ammonia from the elementary elements N and H in the presence of the proper catalyst. By 1913, BASF had a plant making ammonia at the rate of 30 metric tons per day. This success would not have been possible without the work of Alwin Mittasch (who found a commercially satisfactory iron-based catalyst) and of the talented engineer Carl Bosch (who designed the equipment suitable to conduct the reaction at high pressure on an industrial scale)¹. After years of efforts, a solution to the problem of artificial fixation of elementary nitrogen was found. The combination of the technical ability to work at high pressures with the selection of an appropriate catalyst worked wonders. The metal catalyst, present in a different state of matter than the reactants, was able (under adequate pressure conditions) to adsorb and

¹Fritz Haber was awarded the Nobel Prize in Chemistry in 1918 for the discover of ammonia synthesis, although he received it two years after World War I was over, in 1920. This was not without a certain amount of controversy because of the help the process had been to Germany for the production of explosives during World War I and because of Haber's active role in the production of poison gases to be used in the war. Carl Bosch also received the Nobel Prize in Chemistry in 1931 for his contributions to the invention and development of chemical high-pressure methods

dissociate molecular nitrogen into adsorbed nitrogen atoms, which afterwards could react with hydrogen to form the desired ammonia. To give an idea about the importance of ammonia for human demands, it suffices to say that today's annual production is about 120 million metric tons.

This is just an example of the relevance of heterogeneous catalytic processes. Nowadays it can be said that these processes affect almost all aspects of our lives (e.g. they are used in the production of medicines, in the processing of foods, in the refining of petroleum, in the removal of harmful compounds from car exhaust, etc). However, as in the case of the synthesis of ammonia described above, progress in heterogeneous catalysis are often accomplished after exhaustive trial-and-error investigations. This implies an undesirable waste of time and money. In this respect, considerable efforts have been made to gain a deeper understanding of the science underlying heterogeneous catalytic processes, in the belief that this would help to design new and/or improved catalysts. By the early 60's the advent of ultra-high-vacuum techniques allowed the development of new surface-sensitive analytical techniques (such as low energy electron diffraction and electron spectroscopy), and real advances could be made in this direction. Since then the surface science community has worked intensely to relate the atomic-level understanding of heterogeneous catalysis to macroscopic properties such as catalytic activity, selectivity, etc.

As heterogeneous catalysis involves the interaction of reactants at the surface of a catalyst, a large number of these investigations have been performed with idealised catalyst surfaces such as single crystal surfaces. One example of how UHV-based surface science studies carried on single crystal surfaces can lead to a detailed understanding of a catalytic reaction is provided by the fine work of Ertl and collaborators on the ammonia synthesis reaction on Fe single crystals [1–3]. The rate of ammonia production is limited by the initial chemisorption and dissociation of molecular nitrogen, which is structure-sensitive, being two orders of magnitude higher for the (111) face. Actually, structural studies have shown that the catalyst prepared by Mittasch, back in 1909, preferentially exposed (111) planes at the surface [4]. The work by Ertl et al. concluded that dinitrogen needs to adsorb in specific sites that exists in the (111) face of Fe (but not in the (100) and (110) faces) in order to dissociate. This example stresses the importance of the reactants' adsorption sites in the catalytic activity. Indeed, solid surfaces provide atomic ensembles for catalysis difficult to reproduce with discrete molecules, and that is one of the keys to the success of heterogeneous catalysis.

There are several surface science techniques that are sensitive to the adsorption site of adsorbates on surfaces. Among them is the photoelectron diffraction technique in its *scanned-energy* mode. In photoelectron diffraction core level electrons of adsorbates are emitted and partly scattered off surrounding atoms. The interference of the directly emitted wave with its elastically scattered components causes modulations in the photoelectron intensity as a function of emission energy and angle. These modulations carry information about the local structure of the surroundings of the emitter. Measuring the

photoelectron diffraction spectra of the various atoms within an adsorbate allows us to determine the local adsorption geometry.

The present work is concerned with the study of the adsorption structure of some model adsorbate-substrate systems by means of the photoelectron diffraction technique in its scanned-energy mode. Chapter 3 of this thesis is devoted to the study of the adsorption structure of weakly chemisorbed molecular nitrogen on a Ni(100) surface. Although this system lacks any catalytic interest, we deal here with one of the fundamental aspects of the interaction between molecules and surfaces, the relation between bond length and bond strength. The results presented in this chapter are in contradiction with the general idea that associates long bond lengths to weak bonds. Moreover, this study could help to understand the singular electronic properties of this system, that are reflected in the “giant” satellite that appears in the N 1s photoemission spectra. Different theoretical studies have tried to interpret the N₂-Ni(100) bonding, giving different descriptions of the electronic ground state of the system, in which corresponding bonding distances are quite different. The accurate structural information provided here should be taken into consideration in any future theoretical attempt to describe the chemical bond between the dinitrogen molecule and the Ni(100) surface.

Chapter 4 covers the structure determination of the TiO₂(110)-(1x1) surface after reaction with formic acid (HCOOH). This is a model system for the photocatalytic oxidation of organic harmful compounds present in the air and in waste water. Despite the experimental and theoretical efforts that have been invested in the study of this system, some important questions remained unanswered: The presence (or not) of various formate species adsorbed in different sites of the TiO₂(110) surface, and the question of what happens to the proton of the carboxylic group once the formic acid dissociates upon adsorption. We have successfully answered both questions. The results of this chapter show clear evidence for the coexistence of a single formate species (HCOO⁻) and a hydroxyl group (OH⁻). Moreover we have determined the local adsorption structure of both coexistent species. We want to stress the significance of this study since, in common with other oxide surfaces, there are very few quantitative structural studies of adsorbates on titania surfaces, mainly because of the difficulty that usually accompanies the use of the relevant techniques for oxides surfaces studies.

Chapter 5 describes studies of the adsorption structure of the S-enantiomer of α -alanine (NH₂CHCH₃COOH) adsorbed on a Cu(110) surface. Our interest in this system stems from previous work carried out by our group on the non-chiral amino acid glycine (NH₂CH₂COOH) adsorbed on the same Cu surface. We wanted to profit from the knowledge acquired in these studies and try to get insight into the possible differences arising from the chiral nature of the α -alanine molecule. Under certain conditions glycine presents a (3x2)pg surface phase with a glide plane, the appearance of which can be understood in terms of the formation of heterochiral domains. One of the structural phases that results from the adsorption of α -alanine on Cu(110) also shows a nominal (3x2) LEED pattern with some missing half-order diffracted beams. However, due to the chirality of the molecule (which renders impossible the formation of heterochiral domains) these

missing LEED beams cannot be associated with the presence of a glide plane in this case. The results presented in this chapter suggest that the adsorption of the S-enantiomer of α -alanine causes a certain reconstruction of the Cu(110) surface that might explain the appearance of a pseudo-glide plane, although the results presented here regarding the long-range ordering are not entirely conclusive. In addition to this, the study of α -alanine adsorbed on Cu(110) is interesting as a model system for heterogeneous enantioselective catalysis. In this kind of catalysis, chiral molecules are used as modifiers of the surface of conventional metal catalysts to achieve the production of the optically pure enantiomeric forms of a certain substance. In this respect, we outline at the end of chapter 5 a possible method to distinguish between adsorbed enantiomers of a chiral molecule.

In chapter 2 we give some experimental details which will help the reader to gain a better understanding of the topics discussed in chapters 3, 4 and 5. Chapter 6 summarises the main results of this thesis and discusses possible further work.