Chapter 1

Introduction

The human life in its present form is governed by various processes in different circumstances. Familiar examples are *e.g.* the photosynthesis, burning of fossil fuels, corrosion, metabolism and energy consumption of the body in general *etc.* Many of these processes have their origins at the microscopic level, in reactions which occur at the atomic scale via the chemical interaction between the active groups of materials. Thus the macroscopic outcome of the initial products is ultimately settled by the interaction of the microscopic intermediate reactants.

In the chemical industry the goal is often to transfer materials into different materials to obtain the wanted end product or products. Often the reactions needed are far too slow or even energetically unfavourable without external influence. A common practise to direct and assist the wanted reaction is via *catalysis* *i.e.* using a material – catalyst – which does not actively take part in the reaction but provides a bedding for the reactants and shifts the balance or energetics of the reaction controllably. Please notice however that this traditional definition of a catalyst is reshaping as evidence has been appearing of an active participation of the catalyst during the interaction of the reacting materials with the catalyst. Thus a reformulation of the definition of a catalyst is to call as such the solid which does not wear, or get consumed, during the reactions. For an excellent overview of catalysis please refer to the books by Ertl, Knözinger and Weitkamp (1997).

The real catalysts used in the industrial processes are subjected to many economical and practical requirements: The active area of the catalyst must be large but the catalytically active material can be costly and thus a minimal volume or mass must provide as large an active surface as possible – as the catalytic processes occur at the surfaces of the catalyst – and the active material is thus located on the catalyst support, which usually is inactive for the reactions but cheaper and available in large quantities; the reactions are usually driven at high temperatures and gas or liquid pressures, and the catalyst must remain operative for long operation times; therefore the impurities in the intake materials already in extremely low concentrations, *e.g.* 10^{-10} impurities per reactant will, at a pressure equal to that of the atmosphere, try to attack the surface area of 1 centimetre × 1 centimetre approximately at the temperature of 600 K, and so roughly 100 000 impurities would adsorb in one second assuming a probability for sticking of 10^{-8} per trial, and soon the catalytically active surface would be covered with the impurities unless the catalyst is unreactive towards the typical impurities, *e.g.* in residual gases the carbon monoxide, water *etc*, or has an efficient way to remove the impurities via desorption, reaction to side products or other means. The catalyst must also stand demanding mechanic conditions like the wear, cracking and heat convection; these must be taken into account when theoretically modelling the real catalyst.

Typical catalytically active materials are the transition metals – they are the elements located centrally in the Periodic Table – as they have a partially filled *d* shell as the outer-most electronic orbitals; thus they are chemically reactive with these rather localised and directed *d* states, but are still strongly bound and closely packed in larger solid particles like clusters, thin films and bulk materials, and due to the directional bonds geometrical modifications like phase transitions between different lattice structures do not occur easily despite the multiple energetically close phases. The chemically significant electronic structure can furthermore be fine-tuned by the variety of the transition metal elements with a slightly differing filling of the *d* shell.

In addition to the basic catalytic material the reactivity and selectivity for the wanted end products can be improved with additives called promoters, which modify either the electronic or geometrical structure of the surface of the catalyst. Often used promoters are the alkali metals and rare earth elements, placed at the two left-most columns in the Periodic Table. They have rather loosely bound *s* electrons as the active valence, making bonds to other atoms, outside a closed and inter shell. Therefore these elements have high electro-positivity as seen also in the low ionisation energy of them, and with other materials they form easily bonds or hybrids where the charge of the *s* state is partially moved to the more electro-negative substance.

The other group of additives with the opposite tendency are the electro-negative ad-species; they often prevent the desired reaction or the sticking of the reactants by either electronic modification or geometric site blocking, the latter making otherwise feasible sites at the surface inaccessible to the reactants. The atomic oxygen and sulphur are examples of such inhibitors since they form strong bonds with most metallic elements and are always present as impurities in residual gases. Yet often the oxygen is one of the reactants for a wanted reaction and thus its presence is even preferential like serving as the reservoir of atomic oxygen in the process of oxidation of the carbon monoxide (Böttcher *et al*, 1997) or stabilising the alkali promoter against wearing by oxygen in the iron-based catalysts for the synthesis of ammonia (Paál, Ertl & Lee, 1981; Altenburg *et al*, 1980).

From the considerations above and the large amount of different possible materials and reaction conditions it is evident that the optimisation of the catalytic output is a demanding and complicated task. The efficiency is eventually measured as the macroscopic output, but a guide and an implication for the choice of the conditions would be gained from the knowledge of the microscopic steps of the reactions, including the intermediate phases, reaction barriers and potential energy surfaces, effect of the promoters and inhibitors *etc.*

However at the industrial scale, or even down-scaling the catalysts to smaller length scale, there are few and even they not very detailed methods which can provide information on the different steps during the reaction, or *in situ*. Thus simplifications are called for, and they are often done in two different ways: *i*) measuring the catalyst properties either before or after the reaction in an ultra-high vacuum where impurities, which are not present during the reaction either, do not cover the catalytic surface, or in a low pressure of the reaction gases, and *ii*) simplifying the composition of the catalyst. These categories are not exclusive, for example high-pressure studies can be performed on the simplified catalysts. The limitations lead to the famous questions about the validity of the conclusions derived from the simplified studies to the real catalysis across the *pressure* and *material gaps*. Recently there have appeared sophisticated studies *e. g.* from the groups of Gerhard Ertl and D Wayne Goodman which link the low-pressure, simplified measurements to the high-pressure, realistic catalysts and demonstrate the transferability of the results from the model to the practical conditions, thus bridging the material and pressure gaps; an example is also the simple model of Stoltze and Nørskov (1985) who showed a direct relationship between the results from measurements on the clean iron surfaces in the ultra-high vacuum and the iron-based industrial catalysts in the synthesis of ammonia. However there are examples where the connection between the two extremes is not that simple: For example the promoter potassium is believed to form facets of the highly reactive (111) orientation of iron during the reaction conditions of the synthesis of ammonia on the iron-based catalysts, and the high on- and sub-surface coverage of oxygen during the oxidation of the carbon monoxide is achieved by the continuous high-pressure dosing of oxygen to the catalyst during the reaction. Thus the relevance of the results obtained at the simplified conditions is not necessarily straight-forward or even possible.

The ways of analysing the catalysts becomes easier with the simplifications above, and if the optimisation of catalysts in the industry itself is labelled as development the research done at academic institutions can basically be divided into two categories of applied and basic research, whose border-line however is weakly defined. The level of the simplifications is higher in the basic research approach and thus the relevance of the basic research is mainly in improving the understanding of the microscopic mechanism of the catalyst, and the applied research links the basic research and the industrial catalytic plants. The field of basic research which can provide the details of the processes occurring at the catalyst is the surface science. Please notice that the surface science of course covers also many other fields beyond the catalysis, *e.g.* the growth of thin films and high-purity lattices. The characteristic length scale of phenomena at the surfaces goes down to the size of atoms which is less than one millionth of a milli-meter, and the typical times are as fast as pico-to femtoseconds *i.e.* $10^{-12} \ldots 10^{-15}$ seconds. The methodological arsenal of the surface science can capture the finesse of even these high demands; however most of them require a very good, the ultra-high vacuum – *UHV* – in order to avoid impurities from gathering to the surface under study and to avoid the test particles – usually photons, electrons, light atoms or atoms desorbing from the surface – either when approaching or emerging from the surface from interacting with the residual gases. Typical methods include vibrational and electronic spectroscopies, diffractive methods, scattering of light atoms, microscopies *etc.* Several of these approaches are usually needed to form a unique picture of the microscopic structure and dynamics of a system, but even then there remain deficiencies. This is because in few cases the methods listed above can provide a direct and unique outcome of the target but methods by themselves require modelling of the interaction and information carried by the appearing test particle, the methods need a statistics from often an ordered phase of the atoms on the target, or the probe might cause modification of the target.

Therefore comparisons to results from theoretical studies which require as little or preferentially no input from measurement can reliably help further to pin-point and explain the atomic-scale details of the reaction channels, inter-mediate species, interaction of reactants with the different inhibitors and promoters *etc.* Such methods exist but they are in general very tedious as the interactions among the reactants, substrate and additive species are mostly due to chemical bonds formed by the electrons which are distributed between the atoms, and treating the electrons explicitly results in a complicated many-body problem although all the interactions at these length scales are due to the electro-static force, simple in its form. The increase in the computer power in the last decades has however made possible the numerical simulations of configurations of atoms where the electronic structure is solved from the Schrödinger equation or its derivative, and the methods which can yield also accurate forces on the atoms can easily in addition to the electronic structure provide either the static, ground state atomic positions or the realistic dynamics according to the equations of motion. The methods, which can provide accurate energies and electron structures for ensembles of many electrons, include the various approaches in quantum chemistry, the density functional theory and the quantum Monte Carlo method. However even the least costly method for large systems in terms of the computational time required, the density functional theory, can nowadays routinely be used for systems reaching up to tens, in the easiest cases hundreds, of atoms on the most powerful present-day computers. Thus clearly these methods are restricted to only small regions of the potential energy surface, which gives the energy as a function of the atomic coordinates and possibly must include also the electronic excitations and other complex phenomena, of the adsorbate structures and reactions on surfaces, and the achieved microscopic parameters can then be used *e.g.* to model the reaction dynamics or to explain and to some extent predict the experimental results. It is necessary to study the accuracy of the methods, since for example even when the strict density functional theory is in principle exact, the practical formulations are forced to include some approximation, in addition to the numerical inaccuracies involved. The electronic structure calculations on surfaces have so far concentrated on the atomically flat, highly ordered surfaces or clusters modelling them, but recently also *e.g.* the properties of zeolites, which have hollow structures and thus provide a wide surface area to reactions, have been accessed also.

This work belongs to the category of the basic research. Our main purpose is to expand the knowledge of the mutual adsorbate-adsorbate and the adsorbate-substrate interactions via realistic calculations employing the density functional theory on structures modelling the flat, high-index surfaces of transition metals. The main classes of adsorbates in our studies contain the important molecule namely carbon monoxide, the promoter cesium, which belongs to the alkali metals, and to some extent also the oxygen, which is an inhibitor. The present work will also incorporate several previously unexplored entries to the forming database in the literature which gives the community of surface scientists an impression of the accuracy attainable with the present density functional methods.

The present work first includes a short introduction to the density functional theory in the minimal extent in order to understand the computational approach used to obtain the results presented in the following Chapter; a longer and more thorough presentation is unfortunately not feasible within the restrictions on the length of the present form. Some details of the developments achieved by the author are included in the Appendix. We also give a list of the quantities which have been extracted from our calculations. The results are classified into two groups according to phases of single adsorbates and co-adsorbed structures; at the end the results shall be discussed in light of the present knowledge of the systems under study. Regrettably also the Chapter on the results can contain only a part of the results acquired during the course of the activities for the present work. A short summary will out-look the importance the present work. Atomic units are used in the equations unless otherwise mentioned.