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**Reactions of Organic Molecules on
Metal Surfaces studied by STM.**



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Reactions of Organic Molecules on Metal Surfaces studied by STM.

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Abstract

Two distinct systems of surface reactions involving complex organic molecules were studied on single crystal metal surfaces by Scanning Tunneling Microscopy (STM), Low Energy Electron Diffraction (LEED) and X-ray Photoelectron Spectroscopy (XPS) under ultra high vacuum conditions.

The first system focused on the Pt-cinchona alkaloid system, which is a powerful catalytic system in the field of enantioselective heterogeneous catalysis. Herein, an achiral reactant molecule is hydrogenated over a cinchona alkaloid modified platinum surface. Due to the modification of the surface with the chiral cinchona modifier, the symmetry of the system is broken and enantioselectivity is introduced. The hydrogenation of the reactant therefore is biased and leads to an enantiomeric excess (ee) of one enantio form of the product.

The aim of the present STM study was to gain direct insight in the molecular processes which occur during adsorption of such modifiers and reactants. Therefore, the adsorption of cinchonidine (CD), cinchonine (CN) and 2,2,2-trifluoroacetophenone (TFAP) was investigated on both Pt(111) and Pd(111) single crystal surfaces in the presence and absence of hydrogen. Different adsorption modes were identified and a change in adsorption geometry upon addition of hydrogen was followed. The findings are discussed in the light of catalytic, theoretical and spectroscopic data available for this system. Our work showed, that the discrimination of different surface species by their mobility and the time-resolved observation of their surface chemical processes by STM provides a powerful tool for the investigation of complex catalyst systems. These studies can complement other surface analytical methods and quantum chemical calculations in order to gain insight into the mechanistic aspects.

The second system is an example how surface reactions can be used to convert large organic molecules subsequent to their deposition in order to efficiently self-assemble larger structures. For this purpose a perylene derivative, 4,9-diaminoperylene-quinone-3,10-diimine (DPDI), was deposited on a Cu(111) single crystal surface and investigated by STM. These highly mobile precursor molecules are then transformed via a thermally induced surface-assisted dehydrogenation reaction by annealing in-situ at 300 °C. The resulting molecules form autocomplementary species of hydrogen-bond donor and acceptors and thereby can interact with each other via H-bonding. Depending on the surface concentration prior to annealing different well-order molecular patterns are created.

The most stable structure among these molecular patterns is an open hexagonal structure. Due to an exact register with the Cu surface and due to a strong so-called resonance-assisted hydrogen-bonding (RAHB) this highly robust and porous structure is well-suited for the incorporation or trapping of guest molecules. Trapping and manipulation experiments of C₆₀ and octaethylporphyrins (OEP) inside the network are presented and discussed.

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Abbreviations

AFM	Atomic Force Microscopy
ATR-IR	Attenuated Total Reflection Infrared Spectroscopy
CD	Cinchonidine
CN	Cinchonine
DFT	Density Functional Theory
DOS	Density of States
DPDI	4,9-diaminoperylene-quinone-3,10-diimine
ESCA	Electron Spectroscopy for Chemical Analysis
HOMO	Highest Occupied Molecular Orbital
LDOS	Local Density of States
LEED	Low Energy Electron Diffraction
LUMO	Lowest Unoccupied Molecular Orbital
ML	Monolayer
OEP	Octaethyl Porphyrin
OLED	Organic Light Emitting Diode
PTCDA	Perylene-3,4,9,10-tetracarboxylic-dianhydride
PES	Photoelectron Spectroscopy
STM	Scanning Tunneling Microscope
STS	Scanning Tunneling Spectroscopy
TFAP	2,2,2-Trifluoroacetophenone
UHV	Ultra-high Vacuum
UPS	Ultraviolet Photoelectron Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XSW	X-ray Standing Wavefield

1 Introduction

1.1 Motivation and Outline

Since the beginning of science, when there were only the four elements earth, air, fire, and water to distinguish, one was not only interested in the description of these elements, but rather in their interaction. Soon the investigation of reactions alone turned into the very prospering scientific field of chemistry. The impact of chemistry on technology and daily life was always strong and is nowadays stronger than ever: for example if one imagines the huge differences between a world before the emergence of synthetic materials and the world to day. These synthetic materials are the product of organic chemistry.

Most organic synthesis is normally performed in solution, which is reasonable because the physics of chemical reactions are governed by coulomb interactions of the participating atoms or molecular units. In contrast to gravitational interactions which are a typical bulk feature, these coulomb interactions are mediated through the surface of matter. Nevertheless, a lot of matter on earth is solid and chemistry on solid surfaces is central to many areas of practical interest such as heterogeneous catalysis, tribology, electrochemistry and materials processing. With the rise of surface sensitive techniques in the past decades [1], a lot of information and knowledge has been gathered on surface reactions. The adsorption and reaction kinetics of simple inorganic molecules of catalytical systems were extensively studied on single crystal model surfaces [2]. Especially the field of catalysis related surface science studies blossomed, because the industrial need for efficient chemical processes with both low energy consumption and low environmental impact has stimulated the quest for improved catalytic systems.

However, there are huge differences in reactions on surfaces compared to reactions in solution. First of all, the chemical reaction process on surface includes additional reaction steps. Reactants involved in a surface reaction in a first step have to adsorb on that surface and can even adsorb in a variety of different adsorption modes among which only a certain fraction is the chemical active adsorption mode. Furthermore, this first adsorption step is perhaps only an intermediate state for a reactant as e.g. H_2 , which further on has to dissociate to become chemically active. In a second phase the reactants have to meet on the surface that the reaction can proceed at all. In many systems this involves a specific place on the surface, the so-called active site [3], e.g. a step edge or a kink site along a step edge. Diffusion and by that complex molecule-substrate interactions play hence an important role during this step. Additionally, these molecule-substrate interactions may also lead to conformational changes of the reactants upon adsorption or may even induce surface reconstructions caused by the adsorbates.

Because the atoms of organic molecules are covalently bond, all chemical reactions have to entail bond forming, bond breaking or both. The actual reaction pathway therefore often involves a certain attack step where geometrical or sterical aspects play an important role. For example a π -double-bond can not be attacked by a substituent in the nodal plane of its constituting p -orbitals since they do not have any probability density in this plane. Due to the

restriction to two dimensions for reactions on a surface, steric hindrance is of more importance than in solution where the reactants can arrange freely in three dimensions. Therefore the conformational flexibility of larger molecules [4] plays an important role to overcome such steric hindrances. On the other hand, as will be seen in the Pt-cinchona chapter of this thesis, this conformational flexibility may also cause difficulties for experimental methods like STM in terms of resolution.

Finally, the reaction product has to desorb from the surface and its adsorption strength competes with the adsorption strength of new reactants, which try to adsorb on the surface, slowing down or even hindering this adsorption process. Also side products of the reaction might hinder the adsorption of new reactants. In catalysis this is known as poisoning and is a major issue for the longterm efficiency of a catalyst.

Only very recently, surface science studies in this field have been expanded to the study of the chemistry of relatively complex organic molecules on surfaces, in large measure in connection with the selective synthesis and catalysis of fine chemicals and pharmaceuticals (for an extensive review see Z. Ma and F. Zaera [5]). Although the major advances of catalysis were a consequence of mostly empirical trials, advances in the scientific understanding of catalytic systems contributed to further improvement. Therefore the motivation for the work presented in chapter 3 was to further complete the scientific picture of such a complex catalytic system, namely the Pt-cinchona system. This heterogeneous catalytic system can be used for the enantioselective hydrogenation of achiral reactants.

Another strong motivation for research in the field of organic molecules and organic reactions on surfaces is the fascinating idea of molecular electronics. In 1974 Aviram and Ratner proposed a rectifier consisting of a single molecule [6] and thereby marked the laying of the cornerstone of molecular electronics. They suggested that a molecule with a donor-spacer-acceptor structure would behave as a diode when placed between two metallic electrodes. With its basic ideas already established by Feynman in 1960 [7] molecular electronics seeks to use individual molecules to perform non-linear electronic functions as e.g. rectification, amplification or storage. Herein, the necessity of non-linearity for most electronic devices excellently coincides with the non-linearity of quantum mechanical effects which rule the physics of nanoscale systems.

For the same reason of non-linearity of quantum mechanical effects an important point is the reproducibility of such nanoscale systems in order to exactly define the energy levels involved in the functional mechanisms. Organic molecules are made up of covalently bond atoms and are therefore well-defined atomic systems. To use organic molecules as basic building blocks of molecular electronics thus is a natural choice because large amounts of organic molecules can be repeatedly produced with an exactly defined number of atoms and chemical structure. Additionally, the electronic properties of organic molecules can be fine-tuned by variation of certain substituents. A final step along the road to molecular nanoelectronics is then the ability to order the single devices into hierarchical structures forming an electronic circuit. Such ordering processes must follow the same reproducibility and scalability rules known from classical semiconductor electronics in order to be of technological relevance.

In this context it can be very interesting to investigate how reactions of organic molecules can be used to build up higher hierarchical structures by self-assembly [8] on a surface. For this purpose the STM is an invaluable instrument, because it uses the 3rd dimension perpendicular to the surface for an investigative access to the planar molecular structures and reactions on the atomic scale. The fact that STM creates a real-space image of the surface also excellently supports the investigation of sometimes complex hierarchical structures.