Chapter 6

Summary

This thesis includes the local structural determination by means of photoelectron diffraction in scanned-energy mode of three different molecular adsorbates on metal and oxide surfaces. In chapter 3 we have determined the structure of the Ni(100)c(2x2)-N_2 weak chemisorbed system by using chemical-shift photoelectron diffraction in both ends of the molecule, which allowed us to determine the position of both N atoms with a high degree of accuracy. The nitrogen molecule is found to adsorb atop surface Ni atoms with the N-N axis perpendicular to the surface, and a intramolecular N-N bond distance of 1.13 ± 0.03 Å. The results of this study regarding the N-Ni bond distance, which has a value of 1.81 ± 0.02 Å, differ considerably from those of the only previous quantitative structural study on this system [37], and are in clear controversy with the general view that weak chemisorption leads to significant large bond lengths. We have also study the photoemission structure of the giant satellite that appears in the N 1s photoemission spectrum of this system. Our results are consistent with earlier XPD experiments [30] based on the assumption that the satellite peak is separable into components that are fully localised on the two inequivalent N atoms.

In Chapter 4 we have studied a model system for photocatalytic oxidation of noxious organic compounds. We have unambiguously determined the local adsorption structure of the reaction products of formic acid over a TiO_2(110)-(1x1) surface. A single formate species is found to be adsorbed aligned along the [001] bridging an adjacent pair of surface 5-fold coordinated Ti atoms with the formate O atoms near-atop the Ti atoms and with a Ti-O bond length of 2.08 ± 0.03 Å. The proton resulting from the decomposition of formic acid upon adsorption is found to be bounded to bridging-O atoms, which as results of this have a bond length to the Ti underlying atoms of 2.02 ± 0.05 Å, significantly longer than for the bridging oxygen atoms on the clean TiO_2(110)-(1x1) surface. Our results exclude the possibility of a large fractional occupation by the formate species of a second site azimuthally rotated by 90° and bonded to a surface oxygen vacancy site, as proposed in some earlier infrared and X-ray absorption spectroscopic studies.

Chapter 5 covers the study of the adsorption of the S-enantiomer of α-alanine on a Cu(110) surface. The results show that the molecule is adsorbed in a tridentate manner, via the N atom of the amine group and the two oxygen atoms of the carboxylate. The N atom is found to be adsorbed almost on top of a single Cu atom in the first layer of the substrate, while the O atoms occupied inequivalent adsorption sites with a significant offset along [001]. The Cu atom bonded to the O atom of the carboxylate placed opposite to the N atom with respect to the C-C backbone moves towards the Cu atom bonded to the other O atom, so that the Cu-Cu distance along $[1\bar{1}0]$ is shortened by an 11 %. We have also discussed briefly the possibility of using the circular dichroism shown by the angular distribution of photoelectrons from core levels of the alaninate to distinguish between enantiomers of the same chiral molecule, but no definitive conclusion was drawn from this discussion.

As to the work to be done in a near future, many other interesting adsorbates on titania surfaces may be studied. In this direction, we have already performed some experiments regarding the adsorption of water on the TiO_2(110)-(1x1) surface. Water adsorption on this surface may be in the molecular form (when performed at low temperatures), but dissociation at the oxygen surface vacancies may occur if the substrate temperature is high enough to allow the water molecules to diffuse on the surface, so they can reach these vacancies. Another subject of interest is the study of vanadium oxides thin films grown on TiO_2 surfaces. Vanadium oxide films grown on TiO_2 supports show higher reactivity and stronger selectivity in catalytic reactions as compared to those encountered by the individual oxide components. We have also performed some work regarding the characterisation of the growth of different vanadium oxides on the TiO_2(110) surface as a function of preparation conditions, but this work is still in a preliminary stage.

Regarding the identification of chiral enantiomers adsorbed on metal substrates, we will further analyse the CDAD data obtained for the alaninate and glycinate adsorbed on Cu(110), in order to exploit this technique also as an additional tool to obtain further structure information on other parts of the molecule. As to the bottom-up approach followed to understand the bonding to metal surfaces of more complex organic molecules, the next step could be to study the adsorption of di-S-alanine on Cu(110), which has recently shown long-range ordered structures at the coverage regime of 1 ML [175].

In the introduction of this thesis, we justified the study of adsorbates on surfaces by claiming the possible relevance that surface science studies may have in heterogeneous catalysis, and in particular in the development of new and/or improved catalysts. The reader may therefore argue that from our work, based on the study of model systems, not much has been achieved in this direction. Indeed, this is a common argument used to undermine the relevance that the extensive surface science studies of model systems may have to realistic catalytic ones. Substantial efforts are currently being carried out to overcome the two main impediments, namely the so-called *pressure* and *materials* gap, that conventional surface science has to face in its attempt to fully understand real catalytic processes.

A fine example on bridging the pressure gap by using traditional surface science techniques is provided by the study on the CO oxidation over Ru ([176] and references therein). Under UHV conditions Ru is a poor catalyst towards the CO oxidation, while under high pressure and oxidasing conditions it has the highest activity within the platinum-group. A combination of STM, and LEED investigations, together with DFT calculations on the Ru(0001) model system has revealed that this turnover of the reaction rate is due to the formation of RuO_2 patches that growth epitaxially with their (110) plane parallel to the Ru(0001) surface.

Moreover, new experimental approaches that do not require the use of UHV technologies have been in continuous progress. Besides the scanning-tunnelling-microscopy (STM) and its close counterpart, atomic force microscopy (AFM), optical techniques as reflection-absorption infrared spectroscopy or second-harmonic and sum-frequency generation are now available for in situ studies of catalytic processes.

Attempts to bridge the materials gap have led to the development of model catalyst that are similar to industrial catalysts in their complexity, but still suitable for modern surface analytical techniques. These model catalyst consists of metal clusters of a nanoscale size. Some of these nanoclusters preferentially exposed well-defined facets , and in some cases their behaviour may emulate that of their single crystal counterparts.

We hope that the ‘new’ surface science will profit from the basic knowledge that is still acquired with conventional surface science experiments conducted in UHV and with model systems as those reported in this thesis.