Model studies of hydrogen reactivity and production on metal surfaces
A K.
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1. Introduction

1.1 General overview

Hydrogen is considered as a good candidate for limiting the environmental impact of the growing energy demand. It can be used as a clean energy vector for feeding fuel cells and can be obtained from renewable energy sources. In order to properly develop the technologies which are actually needed for supporting an hypothetical future hydrogen economy, great research efforts are necessary in the framework of material science. Production, storage and burning of the fuel are indeed based on catalysis and, more generally, on the chemical and physical properties of metals when exposed to hydrogen. The present work has been driven by these reasons.

Fundamental experimental studies within the framework of surface science are of core importance for a deep comprehension and a proper description of the chemical and kinetic mechanisms involved in catalytic reactions. Here, a series of experimental studies of hydrogen interaction with metal surfaces and ethanol decomposition for hydrogen production is reported. Model single crystal rhodium, ruthenium, platinum and nickel catalysts have been chosen. These transition metals show indeed interesting useful chemical properties and are already commonly employed as catalysts for reforming, oxidation (Pt, Rh, Ru) and hydrogenation (Ni) reactions, as well as for fuel cell electrode coatings (Pt, Ru, Ni). Considerable work has already been done on H interaction with metal surfaces under Ultra High Vacuum (UHV) conditions. However, hydrogen atoms adsorbed on a surface have weak
scattering properties, high diffusion rates and generally show small cross sections to conventional surface science probes. This makes hydrogen-metal systems hard to study from an experimental point of view. In particular, even the simple determination of the adsorption site for an H atom on a single crystal metal surface is not straightforward. As an example, the H/Rh(100) system, where other surface probes have failed, has been chosen to show that this can be done in principle with the aid of high resolution Synchrotron Radiation (SR) X-Ray Photoelectron Spectroscopy (XPS) of the metal core levels.

A significant limit of UHV surface science techniques is the well known pressure gap: it is known that the chemical behaviour of catalytic systems can change substantially under different pressure regimes. In order to overcome this gap, in the case of hydrogen, atomic sources allow to gain the H2 molecule dissociation energy: in this way more energy is available for surface reactions upon adsorption and absorption, thus reproducing higher pressure conditions where, due to the higher total flux, the overall integral of the Maxwell-Boltzmann distribution tail is not as negligible as under UHV. For these reasons, a thermal cracker atomic hydrogen source has been built and fully characterised within the project of the present work. Model hydrogenation reactions by gas phase H atoms have been studied on Ni(110) and Ru(10\(\bar{1}\)0) single crystal surfaces. Cleavage of the very strong oxygen-Ni bond upon hydrogenation shows the peculiar reactivity of H atoms. On the other hand, the (10\(\bar{1}\)0) surface of ruthenium is very open and allows reaching high hydrogen surface densities, thus being a good template for studying the balance between adsorption and reaction kinetics of H atoms.

Finally, an experimental study of ethanol decomposition on rhodium single crystal surfaces is reported. Efficient catalysts for ethanol steam reforming for “clean” hydrogen production have attracted great attention and in particular new rhodium-based catalysts have recently been developed for this reaction.

1.2 Hydrogen interaction with metal surfaces

The hydrogen molecule presents a strong intermolecular bond (bond length: 0.74 Å [1,2] – gas phase dissociation energy: 4.75 eV [2]) and generally exerts weak van der Waals interactions with a solid surface. However, upon adsorption on most transition metal surfaces, H2 dissociates leading to atomic adsorption. When studying
reactivity parameters, there is an important influence of the kinetic aspects of the hydrogen-metal interaction: an activation energy may exist for the initial dissociation step (activated adsorption) and the kinetic energy generated upon adsorption is somehow dissipated.

Figure 1.1 - Surface interaction potentials as a function of the surface distance $z$ of molecular and atomic hydrogen (Lennard-Jones potential shapes): (a) molecular physisorption; (b) predissociated hydrogen interaction with the surface; (c) description of the spontaneous dissociative adsorption as a superposition of curves (a) and (b); (d) non-activated dissociative adsorption; (e) activated dissociative adsorption.
1. Introduction

This is a key point for our purposes and the use of an atomic hydrogen beam can significantly alter the chemistry of surface hydrogenation reactions, because a consistently higher energy is available and, in parallel, different hydrogenation pathways can be sampled. In the case of activated dissociative adsorption, the energy required to overcome the dissociation barrier (about ten times higher than the average energy of gas phase $H_2$ at room temperature [3]) is generally balanced by the energy gained upon atomic adsorption. This first step can be eliminated and the overall reaction mechanism simplified by using atomic hydrogen beams. The surface interaction energy diagrams for the different adsorption processes are shown in Figure 1.1 [1,4].

The overall energy balance is as follows: the total heat of adsorption ($E_{ad}$) is given by the difference between twice the energy of the H-metal bond ($E_{Me-H}$) and the molecular heat of dissociation ($E_{diss}$). Thus we have:

$$E_{Me-H} = \frac{1}{2} (E_{diss} + E_{ad})$$  \hspace{1cm} (1.1)

Typical values (values can vary depending on surface coverage) for $E_{Me-H}$ are 2.7 eV on Ni(110) [1], 2.8 eV on Rh(100) [5,6] and up to 2.71-2.79 eV on Ru(1010) [7], corresponding to $E_{ad}$ values of the order of 0.7-0.8 eV. Temperature Programmed Desorption (TPD) experiments show indeed that dissociatively chemisorbed hydrogen recombines and desorbs from transition metal surfaces already at relatively low temperatures (just above 100 K) and that the highest temperature desorption states are generally centred in the 300-400 K range.

The coverage dependence of hydrogen adsorption kinetics is not always clear and different mechanisms have been proposed. If the Herz-Knusden equation is assumed as a model for the kinetic description [8]

$$\frac{d\theta_H}{dt} = \frac{2s(\theta)p_{H_2}}{\sqrt{2\pi m_{H_2} k_B T}}$$  \hspace{1cm} (1.2)

where $s(\theta)$ is the coverage-dependent sticking coefficient, both second and first order adsorption kinetics are considered for a proper description of hydrogen adsorption depending on the case. In the former case the sticking coefficient is assumed to be of the form
and well describes hydrogen dissociative adsorption on Rh(111) and Ir(111) for example [1]. On the contrary, H/Ni(111) and H/Ru(0001) [1] systems show the evidence for a first order reaction, where $s(\varnothing)$ may be expressed as

$$s(\varnothing) = s_0 \left(1 - \frac{\theta}{\theta_{sat}}\right)^2$$

(1.3)

When atomic hydrogen is used, more complex mechanisms are involved and new kinetic descriptions are needed in order to properly describe experimental data. This is the case for example of H atoms interaction with Ru(1010), which will be discussed in the present work.

![Figure 1.2 - Schematic potential energy diagram for hydrogen adsorption and absorption on Pd(110). The activation barrier for population of subsurface sites is removed upon induced surface reconstruction [1].](image)

Due to its small mass, hydrogen shows a peculiar behaviour for surface diffusion: quantum mechanical tunnelling effects are involved, which make a pure classical description inadequate. This allows also surface to subsurface hydrogen migration: the process can be both activated or not. In some cases, like palladium for
example [1,9-14], no activation energy is present or the initial low energy barrier is eliminated upon the hydrogen-induced surface reconstruction (see Figure 1.2) [1]. On the contrary, on other transition metal surfaces such energy barrier is too high and hydrogen diffusion into the bulk does not occur, nor hydrogen absorption into subsurface sites. However, on Ni(111), for example, the energy barrier for subsurface diffusion can be overcome when exposing the surface to atomic hydrogen, thus gaining half of the H\(_2\) gas phase dissociation energy per surface H atom. In this way, subsurface sites can be populated and new absorbed hydrogen species are identified by means of TPD and High Resolution Electron Energy Loss Spectroscopy (HREELS) (see Figure 1.3) [3].

![Figure 1.3 - TPD spectra obtained by annealing the Ni(111) surface after exposure of the surface to atomic hydrogen at 80 K (left); potential energy diagram for the H/Ni(111) system (right) [3].](image)

The same behaviour has been observed also when exposing Ni(110) [15] or Rh(100) [16] to atomic hydrogen. In these cases, higher density pure surface hydrogen overlayers can be obtained and subsurface sites are generally occupied in addition to surface states, thus reaching an overall higher saturation coverage for hydrogen (see Figure 1.4).

In addition, both absorbed and gas phase H atoms show peculiar reactivity properties towards surface-mediated hydrogenation reactions with respect to conventional molecular hydrogen [3,17-23]. Several examples are reported in the literature, including simple abstraction reactions as well as efficient hydrocarbon hydrogenation on Ni surfaces.
The comprehension of hydrogen interaction with co-adsorbed atoms or molecules is indeed of primary interest. Most studied catalytic hydrogenation reactions proceed via a Langmuir-Hinshelwood (LH) mechanism, where both reactants are assumed to stick on the metal surface as a first reaction step. Moreover, as already mentioned, hydrogen absorbed into subsurface sites can show a peculiar chemistry towards the hydrogenation of other co-adsorbates [3,19-22]. The mechanisms and the coverage dependence of these reactions can be further explored...

Figure 1.4 – a) H/Ni(110) system: hydrogen coverage as a function of the gas phase H atoms and H₂ molecules exposure, as obtained by TPD [15]; b) the same on Rh(100), where the surface has been exposed to H₂ (triangles), H atoms (squares) and D atoms (full circles) [16].
with the direct use of gas phase H atoms: site blocking effects (two empty adsorption sites for molecular dissociative adsorption are needed) can be overcome and new reaction pathways (Eley-Rideal and Hot Atom kinetics) can be studied, thus simulating new reaction conditions. In particular, the idea of the existence of a hot precursor in the reaction mechanism was proposed in Ref. [24]. In the case of atomic hydrogen adsorption, "hot atoms" are generated through the strong attractive potential between gas phase atoms and the metal surface. A "hot atom" does not directly stick on the surface at a determined adsorption site, but exists in a bound state normal to the surface with a considerable translational energy parallel to the surface (of the order of the eV).

Considerable work has already been done from the computational point of view to characterise this "hot" state. The rate equations which describe the abstraction of adsorbed D atoms from gas phase H atoms through a hot-atom mediated process have already been proposed in Ref. [25]. It was found that, from a pure kinetic aspect, the parameter which governs the process, thus determining the reaction rate, is the ratio between $p_s$ and $p_r$. The former is defined as the probability for hot atom sticking at empty sites, while the latter is the probability for hot atom reaction with adsorbed species. Quasi-classical trajectory studies [26], molecular dynamics approaches [27] and classical mechanics together with potentials obtained from the Embedded Atom...
Model (EAM) [28] have been used for a better description of this reaction process. On Cu(111), it was found that impact of the incident atom close to the adsorbate can lead either to Eley-Rideal reactions or trapping. This latter adsorbate-mediated mechanism becomes relevant for impacts within 2 Å of the adsorbate. Also at larger impact parameters, scattering from the surface corrugation leads to a trapped state. A bound hot atom travels rapidly along the surface at an energy level which can be even 2 eV above the ground state on Cu(111). Rather than being dissipated into the substrate, the excess energy, due to the exothermicity of the subsequent hydrogenation reaction, shows up in the reaction products when considering deuterium abstraction. In Figure 1.5, the calculated average kinetic energy along the surface for a hot atom is shown as a function of the impact parameter $b$. The system which has been considered for this calculation is H (D) on Cu(111). $K_{rel}$ is defined as the relative kinetic energy of the two particles (incident and target atoms) following a collision which leads to trapping of the incident atom. It is shown that two dimensional opacity functions can be evaluated from the reaction modelling. In Figure 1.6, the opacity function for reactive trajectories is plotted for example. The opacity function is in this case the fraction of reactive trajectories at each impact parameter. It has also been proven that hot atoms dissipate their kinetic energy due to unreactive collisions with adsorbed particles. A loss of about 0.1 eV per collision has been estimated on Cu(111) [27]. A detailed analysis of the cross sections for trapping vs Eley-Rideal reactions for H on Ni(100) can be found in [28]: the dependence of the cross sections on the incident atom energy has been studied within the 0.1-1.5 eV collision energy range.

On clean transition metal surfaces, hydrogen generally prefers most coordinated hollow adsorption sites (fourfold and threefold). However, adsorption in bridge sites has also been reported, for example on W(100) [29], W(110) [30] and Fe(110) [31]. Moreover, the adsorption site can change as a function of the hydrogen coverage due to lateral interactions and surface reconstruction. Experimentally, the determination of the preferred adsorption site for H on a surface is a non-trivial task [32]: vibrational techniques are mostly employed (HREELS) and recently it has been demonstrated that for Rh(100) even Scanning Tunneling Microscopy (STM) fails [33].

Chemisorbed hydrogen interaction with the metal surface and lateral adatom forces lead to the formation of several ordered structured on transition metals at low temperatures. In many cases surface reconstruction is also induced. For a general overview see ref. [1].
Figure 1.6 - Two-dimensional opacity function for reactive trajectories. $x$ and $y$ values represent the initial coordinates of the incident atom. The contours reproduce the corrugation function of the Cu(111) surface. The target adsorbate atom hollow site is at $x = 0 \text{ Å}$ and $y = 1.47 \text{ Å}$ [26].

From the computational point of view, hydrogen is the simplest molecule in nature and can be well described; calculations within the Density Functional Theory (DFT) framework for hydrogen-metal adsorption systems have been performed extensively. However, energy differences (for example between non-equivalent adsorption sites) can be very little (of the order of some 10 meV) and therefore difficult to reproduce. This is the case for example of H/Rh(100): hydrogen adsorption and decomposition pathways [34-37], surface induced relaxation [38] and adsorption energies [6,16,39,40] have been calculated intensively, but often theory-theory and theory-experiment inconsistencies have been found due to the high precision required [33]. This can make H adsorption systems still a hard task for surface science both from the computational and the experimental point of view.
2. Experimental and computational background

2.1 Overview of experimental setups and techniques

The UHV measurements reported in this work have been carried out in three different experimental setups, which will be shortly described below. For the present purposes, no details on the working principles of the experimental techniques will be given; instead, only the main descriptive parameters of the used instrumentation will be reported.

2.1.1 General purpose experimental chamber

A general purpose UHV system has been used for reactivity and desorption measurements on rhodium and ruthenium samples. The experimental chamber had a base pressure of $7 \times 10^{-11}$ mbar and was pumped by a turbomolecular, an ion and a titanium sublimation pump. The sample was mounted on a four degrees of freedom manipulator by means of two tungsten wires (diameter ranging from 0.25 to 0.38 mm depending on mounting conditions), allowing resistive heating up to 1300 K and cooling down to 90 K by liquid nitrogen. An ion gun was used for Ar$^+$ surface sputtering. Pure gases where admitted directly into the chamber or could be dosed through a stainless steel tube in front of the sample to avoid vacuum contamination. Low Energy Electron Diffraction (LEED) optics were available. Desorption
experiments were carried out with the use of a Leybold-Inficon Residual Gas Analyser (RGA). Linear temperature ramps were obtained by controlling the heating filaments power supply (Sorensen) with a PID instrument (Eurotherm). The chamber was equipped also with an Electron Spectroscopy for Chemical Analysis (ESCA) facility allowing XPS measurements (Mg Kα single anode 400 W X-Ray source – hv=1253.6 eV, ΔE=0.9 eV – VG MK II electron energy analyser). A home-made atomic hydrogen source of the Bischler and Bertel type (see Section 2.2) has been added to the setup as part of this thesis work.

2.1.2 New experimental setup

A new general purpose experimental setup has been designed, assembled and commissioned. The sample manipulator is mounted on a differentially pumped rotary flange: this design allows off axis movement of the manipulator to different measurement positions (see Figure 2.1).

Figure 2.1 - 3D shots from the CAD projects and picture of the experimental chamber: (a) external view of the chamber with monochromator and electron energy analyser on the left; (b) detailed picture of the main chamber: the μ-metal shields (yellow) and the motor for the movement of the flange (violet) are visible; (c) picture of the final setup during commissioning.
2. Experimental and computational background

Hydrogenation reactions on Ni(110) have been carried out in the new setup just at the end of the commissioning (January 2004). The instrumentation from the previous experimental system (Section 2.1.1), which was dismantled, has been transferred. In addition, a fast entry lock system, a five degrees of freedom fully motorised manipulator, a Spot Profile Analysis LEED (SPA-LEED) and a monochromated Al X-Ray source are available. The Leybold-Inficon RGA was replaced with a new instrument from SRS. Working background pressure is $5 \times 10^{-11}$ mbar. The chamber is pumped by an ion, a titanium sublimation and three turbomolecular pumps.

2.1.3 The SuperESCA beamline at ELETTRA

Part of the experimental work which is reported in this thesis was performed at the SuperESCA beamline at ELETTRA, the synchrotron radiation facility in Trieste (Italy). The beamline is dedicated to soft X-ray photoemission experiments on solid surfaces [41,42]. The light source is a 81 periods undulator (period length = 56 mm) which covers a photon energy range from 85 to 1500 eV (120 to 2100 eV) at a ring energy of 2.0 GeV (2.4 GeV). The experimental station is equipped with a double pass hemispherical electron energy analyser having variable magnification, variable entrance slit and a 96-channels detector. A five degrees of freedom fully computer-controlled liquid nitrogen cooled sample manipulator is available. Alternatively, a manual four degrees of freedom liquid helium cooled manipulator can be used. The monochromator of the SuperESCA beamline is a modification of the standard version of the plane grating SX700 monochromator. The new design has been developed in order to make the SX700 work stigmatically: this is obtained introducing a pre-focusing mirror. At a photon energy of 400 eV, storage ring energy of 2.0 eV and storage ring current of 100 mA, the flux at the sample is $10^{11}$ photons/s with a resolving power ($E/\Delta E$) of $10^4$. Conventional instrumentation for surface science UHV analysis is available in the experimental chamber: a gas line, a sputter gun, an RGA, a LEED and a microchannel-array gas doser are present.
2.2 The thermal cracker UHV atomic hydrogen source

2.2.1 Theoretical background

This kind of UHV H atoms source acts as a thermal cracker and was firstly proposed by U. Bischler and E. Bertel [43]. The doser basically consists of a tungsten capillary (L = 50 mm, i.d. = 0.6 mm, o.d. = 1.6 mm) which is heated by electron bombardment up to 2000 K. Molecular hydrogen flows through the tube and thermally dissociates at the hot tungsten walls. The source can work under UHV due to the low vapour pressure of tungsten, which becomes relevant in a UHV system only for temperatures higher than 2100 K (see Figure 2.2).

![W Vapour Pressure vs Temperature](image)

**Figure 2.2 - Tungsten vapour pressure as a function of temperature: UHV compatibility holds for capillary temperatures up to 2100 K.**

100% cracking efficiency is reached with this method. On the contrary, a simpler widespread way for producing gas phase H atoms is to thermally dissociate H_2 on a hot tungsten filament (2000 K) placed in front of the sample. It is clear that in
Experimental and computational background

the latter way, only a small fraction of the hydrogen is dissociated, depending on the geometry; moreover, the sample is radiatively heated by the filament and spurious evaporated contaminants cannot be avoided. In the Bischler and Bertel setup, a water cooled copper shield is placed between the tungsten tube and the sample, acting both as a shield for radiation and contaminants and as a collimator. An alternative method which is used for producing H atoms beams uses Radio Frequency (RF) cavities to dissociate the molecules [44-46].

The efficiency of the thermal cracker source can be estimated by assuming equilibrium between hydrogen atoms and molecules in the thin doser capillary [47]: this assumption is not straightforward and has to be justified. Experimental measurements of the real cracking efficiency show some discrepancies with respect to the predicted values based on this assumption, however the data can be fitted with this model by correlating the gas flux at room temperature with the gas pressure [47]. So, assuming equilibrium in the capillary,

\[ H + H \rightleftharpoons H_2 \] (2.1)

the partial pressures of hydrogen atoms \( (p_{H}) \) and molecules \( (p_{H2}) \) are determined by the total pressure \( (p) \) and the degree of dissociation \( (\alpha) \):

\[ p_{H} = p \frac{1 - \alpha}{1 + \alpha} \quad p_{H2} = p \frac{2\alpha}{1 + \alpha} \] (2.2)

The equilibrium constant is therefore

\[ K = \frac{[p_{H}][p_{H2}]}{[p_{H2}]} = \frac{4\alpha^2 p}{1 - \alpha^2} \] (2.3)

Since the temperature dependence of the equilibrium constant can be calculated [47-49] and is determined by the numerical equation

\[ \log K(T) = -\frac{23700}{T} + 6.35 \] (2.4)
2. Experimental and computational background

it is possible to calculate directly the degree of dissociation as a function of pressure and temperature

\[ \alpha(p, T) = \sqrt{\frac{K(T)}{4p + K(T)}} \]  \hspace{1cm} (2.5)

At this point, the pressure at the end of the tungsten capillary must be evaluated. For the cold tube (no dissociation), the pressure at the outlet of the capillary can be obtained from the increase of the hydrogen partial pressure in the experimental chamber \[47\]. For typical dosing experiments, assuming a pressure increase in the camber of \(1 \times 10^9\) mbar and a pumping speed of 2500 ls\(^{-1}\), a molecular hydrogen flux of \(8 \times 10^{13}\) s\(^{-1}\) and a pressure at the end of the tube of \(2.5 \times 10^5\) mbar are obtained. Under these conditions, the molecular hydrogen flux through the capillary is given by

\[ \Phi = \frac{Sp}{\sqrt{2\pi mk_BT}} \] \hspace{1cm} (2.6)

where \(S\) is the tungsten tube opening area. Upon heating, the equilibrium changes both due to temperature and dissociation. By imposing the conservation of the mass flux, we have

\[ \frac{m_{H_2} P_{H_2}(300K)}{\sqrt{2\pi m_{H_2} k_B \cdot 300}} = \frac{m_{H_2} P_{H_2}(T)}{\sqrt{2\pi m_{H_2} k_B \cdot T}} + \frac{m_H P_H(T)}{\sqrt{2\pi m_H k_B \cdot T}} \] \hspace{1cm} (2.7)

By using the equilibrium conditions from Equation 2.2 an expression for the tube pressure as a function of temperature and degree of dissociation is obtained:

\[ p(T, \alpha) = p(300K)\sqrt{\frac{T}{300}} \left( \frac{1 + \alpha}{1 - \alpha + \sqrt{2\alpha}} \right) \] \hspace{1cm} (2.8)
Finally, by inserting this relation into Equation 2.5 the dependence of the cracking efficiency from the tube temperature and pressure at 300 K ($p_0$) can be obtained. Solving the third order equation yields

$$\alpha(T, p_0) = \frac{1}{2} \frac{-15\sqrt{2}K + \sqrt{1350K^2 + 240\sqrt{6T}p_0K + 360\sqrt{3T}p_0K + 900\sqrt{2}K^2}}{2\sqrt{6T}p_0 + 15K + 2\sqrt{3T}p_0} \quad (2.9)$$

Experimental data (as obtained by the pressure drop method [47]) and fitting curves with Equation 2.9 are shown in Figure 2.3.

![Figure 2.3](image)

**Figure 2.3** - Experimental data for the source cracking efficiency obtained with the pressure drop method by Eibl and co-workers [47]; solid lines represent the best fit according to the model of Equation 2.9.

The tungsten tube of the Bischler and Bertel atomic hydrogen source can be considered as an effusive source and can therefore be properly described in order to study the angular distribution of the effusing hydrogen. As a first point, the cold tube (no dissociation) is considered, focusing on the case where the length of the tube $L$ is much larger than its radius $R$. The pressure drop in the tube is estimated as a function
of the distance $z$ from the entrance by a complicated expression [47,50] which, for large values of $L/R$, can be reasonably approximated with a linear form. Using the assumption of the linear pressure drop, an analytic form for the angular distribution of the flux can be obtained

$$I(\Theta) = T(\Theta) \cos \Theta$$

where $T(\Theta)$ is the tube transmission function of the form

$$T(\Theta) = \begin{cases} 1 - \frac{2(1-\beta)}{\pi} \left[ \arcsin x + x \sqrt{1-x^2} \right] + \frac{4(1-2\beta)}{3\pi} \left[ 1 - \left( 1 - x^2 \right)^{3/2} \right] , & x = \frac{L}{2R} \tan \Theta < 1 \\ \beta + \frac{4(1-2\beta)}{3\pi} , & x = \frac{L}{2R} \tan \Theta \geq 1 \end{cases}$$

where

$$\beta = \frac{4R}{3L}$$

Figure 2.4 - Calculated angular distribution of the flux at the exit of the cold tungsten capillary: exact solution (left) and linear approximation (right) [47].
2. Experimental and computational background

A plot of the angular distribution obtained in this way for the cold tube is reported in Figure 2.4. It is important to observe that the linear approximation which has been used holds for large values of $L/R$: in the present case $L/R = 150$ and a comparison with the exact solution reveals an error of about 5% in the transmission function [47].

![Figure 2.4](image)

*Figure 2.5* - Experimental (a) and simulated (b) angular distribution of the flux from the end of the tungsten tube in relation to the tube temperature. Direct comparison between experimental data and simulation results after convolution with the detector function (c) [47].
Up to here, no consideration has been given to the fact that the tube is hot and that molecular hydrogen dissociation occurs at the walls. With the aid of some simple assumptions, Monte Carlo simulations have been carried out [47] in order to reproduce the angular distribution of the H atoms flux at working conditions. The tube (total length \( L \)) has been divided into a cold part and a hot part with length \( L_h \): this is in line with the real case, where only the terminal part of the tungsten capillary is effectively bombarded by electrons and heated. At the inner wall of the cold part of the tube \( \text{H}_2 \) impinging molecules leave the surface following a cosine distribution, while at the hot part all the \( \text{H}_2 \) impinging molecules dissociate and both atoms leave the surface independently according to a cosine distribution. Finally, H atoms impinging on the cold part of the tube are assumed to recombine and desorb as \( \text{H}_2 \), while those impinging on the hot part leave the surface again as atoms.

Using these general assumptions, the angular distribution of the effusing particles has been simulated by Monte Carlo techniques (Figure 2.5 b) and compared to the experimental data (Figure 2.5 a) [47]. At \( T = 1860 \text{ K} \) the maximum dissociation efficiency is reached with a hydrogen flux of \( 3.2 \times 10^{13} \text{ mole/s} \). For lower temperatures (1670 and 1570 K), it can be observed that the experimental distribution functions get broader. This is due to the shorter hot part of the tube. In the latter cases, the cracking efficiency is of 52% and 24% respectively. In Figure 2.5 c, the experimental angular distribution is directly compared with the results from Monte Carlo simulations, which have been approximated by an analytic function and then convoluted by the detector function.

In general, at working conditions of the thermal cracker, hydrogen is supplied to the tube entrance at a pressure of the order of \( 10^{-2} - 10^{-3} \text{ mbar} \), while a pressure of the order of \( 10^{-5} \text{ mbar} \) is found at the exit. This gives a flux of about \( 10^{14} \text{ molecules/second} \) at room temperature with a pumping speed of 1800 l/s [47].

2.2.2 Source technical details

A home made atomic hydrogen source of the Bischler and Bertel type was built for the hydrogenation reaction experiments with gas phase H atoms under UHV conditions. The baseline scheme reported in Ref. [43] was followed (Figure 2.6).
Figure 2.6 - General scheme for the construction of the atomic hydrogen thermal cracker.

Figure 2.7 - Pictures of the tungsten tube and its supports before and after source assembling.
The tungsten tube is connected to the hydrogen stainless steel supply tube by a ceramic adapter which provides both electrical insulation and sealing. The W tube is directly connected to an electrode for supplying the acceleration voltage (+1 kV). Two stainless steel tubes act both as water supply for cooling and as a support for the front copper shield. A mechanical shutter was added. A K-type thermocouple is spot-welded to the tungsten capillary via a thin tantalum shield at about 30 mm from the capillary tip. This allows temperature monitoring and PID control: the thermocouple signal has been calibrated once with respect to the real tip temperature measured with a pyrometer. The tungsten filament for electron emission is mounted directly on the back of the copper shield. On the back of the source, a gas reservoir is installed, where an all metal leak valve for hydrogen dosing from a 10 bar bottle is mounted, together with an all metal angular valve for differential pumping and for the evacuation of the reservoir. Details of the assembly and the final appearance of the source can be seen in the pictures taken during the source construction in Figure 2.7.

Figure 2.8 - Pictures taken during the thermal cracker assembling sequence: (a) supports and water cooling circuit; (b)-(c) insulating ceramics and W tube; (d) final outlook.
The whole source is mounted on a standard CF40 flange with five CF16 flanges for thermocouple, filament current, high voltage feedthroughs, water cooling, hydrogen supply and shutter control. A complete sequence of pictures taken during the source assembly phase is shown in Figure 2.8.

Finally, the instrument has been tested: the tube temperature has been measured as a function of the dissipated power (filament emission current x accelerating voltage). The power needed to reach working conditions (Figure 2.9) is very similar to the values reported in the literature [43,47]. With 30 W a 100% cracking efficiency is obtained.

![Figure 2.9 - Capillary temperature (measured with a pyrometer) as a function of the power.](image)

In order to test the source, an indirect measurement of the cracking efficiency has been performed on the basis of the "pressure drop" method [47]. Generally, hydrogen atoms are removed from gas phase in the vacuum system faster than the hydrogen molecules. This is due to the higher reaction rate of atomic hydrogen with the titanium getter films in the sublimation pump and in the ion getter pump. Therefore, the equilibrium pressure established for a pure molecular flux at room temperature will decrease with increasing capillary temperature. Finally, pressure will settle at a minimum value when the cracking efficiency has reached 100%. Indicating the equilibrium pressure at room temperature with $p_{mol}$ and its minimum value at 100% efficiency with $p_{at}$, the degree of dissociation $\alpha$ will be simply determined by the pressure at tube temperature $T$:
2. Experimental and computational background

\[ \alpha(T) = 1 - \frac{p(T) - P_{at}}{P_{mol} - P_{at}} \]  

(2.13)

Pressure has been measured indirectly registering the ion pump current, which is related to the real pressure from calibration data reported in the pump datasheets. Pressure measurement was not performed with ion gauges in order to avoid false signal effects due to the presence of spurious electrons from the source. It can be seen from data reported in Figure 2.10 that, according to this method, 100% cracking efficiency (calculated on the basis of Eq. 2.13) is obtained with this instrument above a tube temperature of 1700 K. This result is in line with data reported in [47] and shown in Figure 2.3.

![Figure 2.10 - Cracking rate as a function of the tube temperature as measured with the pressure drop method (H\(_2\) source pre-chamber pressure: 3\(\times\)10\(^{-3}\) mbar).](image)

In addition, molecular and atomic hydrogen uptakes were performed on a polycrystalline silver sample at 90 K: it is well known that H\(_2\) does not stick, nor dissociate on silver surfaces at this temperature [51]. In the former case, no desorbing hydrogen was detected in the mass 2 TPD spectra; on the contrary, when the sample was exposed to the hydrogen flux from the hot source, H atoms adsorption was observed and a broad desorption peak was detected in the TPD spectra at about 140 K, thus confirming the high efficiency of the doser. Care has to be taken for proper outgass of the tungsten tube after bake-outs (several hours are needed), but a final working background pressure of 2\(\times\)10\(^{-10}\) mbar is obtained.
It has already been reported in the literature [44-46] that H atoms beam parameters have a remarkable influence on the hydrogenation reactions. For example, on Ru(001) different surface hydrogen saturation coverage values can be obtained at low temperature using a microwave discharge source or a simple tungsten filament. This occurs because the saturation is reached when hydrogen adsorption and abstraction reactions balance: the equilibrium is therefore governed also by the gas phase H atoms kinetic parameters [44]. H atoms produced with a thermal cracker of the Bischler and Bertel type have a high translational energy (0.2-0.4 eV); on the contrary, when using RF sources, for example, translational energies of 0.06-0.08 eV have been reported [44]. Moreover, the cracking efficiency of the source can also have an influence: when using a simple hot tungsten filament, only a small fraction of the hydrogen molecules will dissociate. These effects have to be considered and hydrogenation reactions results within a surface science experiment with atomic hydrogen have to be related to the way H atoms are produced. An extensive study of the H beam parameters and their influence on the chemical reactivity has not been done yet: the kinetic characteristics of an atomic hydrogen beam are strictly source-dependent and a tuneable control of the parameters is not feasible.
2. Experimental and computational background

2.3 The UBI-QEP model for the calculation of adsorption energies and reaction barriers

Computational evaluation of the kinetic parameters which govern a chemical reaction is of primary importance for a proper interpretation of the experimental data: comparison between theory and experiment is generally a key point for a better understanding of physical phenomena. Calculation of adsorption energies and geometries, reaction barriers and paths, is best done within the DFT framework: a good calculation accuracy can be obtained, but time expensive and resource demanding efforts are needed. On the contrary, with the use of the simple phenomenological model denominated UBI-QEP and proposed by E. Shustorovich [52-55], rough estimates of the kinetic parameters governing a reaction on a surface can be obtained in short time, providing a loss in accuracy is accepted. In this work, the UBI-QEP model has been used to study the coverage dependence of the hydrogen adsorption energy and coordination on Rh(100) and to evaluate adsorption energies and decomposition barriers for the ethanol molecule on Rh(111).

2.3.1 The UBI-QEP model

The Unity Bond Index - Quadratic Exponent Potential (UBI-QEP) model was developed on the basis of the previous less general Bond Order Conservation (BOC) model proposed by the same authors [52-55]. The Bond Order is a quantum mechanical quantity which reflects the fact that a certain amount of bonding strength is shared among all the bonds involving a given atom; when the number of bonds of the atom is reduced, the strength of each of the remaining bonds increases, thus indicating that the overall bond order is conserved and is redistributed among the remaining bonds [53,56-59].

The Bond Order is a non-observable quantity and has therefore to be correlated with a measurable quantity: one of the most convenient observables is the bond distance or some function of it, like the exponential bond order, for which the conservation to unity has already been verified by ab-initio calculations. If we denote with $r$ the bond distance of a two-centre interaction which has an equilibrium value of $r_0$, then the sum of the bond orders for a many body interaction is conserved to unity and the single pair-wise bond order $x(r)$ can be written as
2. Experimental and computational background

\[ x(r) = e^{-\frac{r-r_0}{b}} \]  

(2.14)

Each of the two-body interactions is described by a Morse potential of the bond order

\[ E[x(r)] = a[x^2(r) - 2x(r)] \]  

(2.15)

and the total energy can be additively obtained by

\[ E(X) = \sum_i a_i[x_i^2 - 2x_i] \]  

(2.16)

In a more general framework, the pair-wise interactions between the adsorbate atoms and the atoms of the metal surface can be expressed as a function of the internuclear distances \( r \): the potential between each of the interacting bodies may be mathematically described as a polynomial functional of the variable \( x(r) \), which will be further generalised with respect to the Bond Order case:

\[ E = \sum_i a_i x(r)^i \]  

(2.17)

By assuming at this point that the potential has a single minimum (which is reasonable for non-dissociative adsorption or desorption) and by putting the reference point for the energy scale at infinite two body separation, the pair-wise interaction energy assumes a quadratic form:

\[ E = a_2 x^2(r) + a_1 x(r) \]  

(2.18)
At the equilibrium, where \( x(r) = x(r_0) = x_0 \), the first derivative of the potential is equal to zero, while the second derivative must be positive: applying these constraints yields

\[
E = a_2 [x^2(r) - 2x_0x(r)]
\]  

(2.19)

With no loss of generality and just by a rescaling of the \( a_i \) constants, the value \( x_0 = 1 \) can be chosen at equilibrium, thus obtaining

\[
E = a_2 [x^2(r) - 2x(r)]
\]  

(2.20)

where now \( a_2 \) is the two body binding energy. The general features of the variable \( x(r) \) are: i) there is a one to one correspondence between \( x(r) \) and \( r \); ii) \( x(r) \) is non negative; iii) \( x(r) \) is monotonically decreasing; iv) at equilibrium \( x(r_0) = 1 \). As the atomic and diatomic wave functions are known to have exponential radial parts (this point will be further discussed in Section 2.3.2), a general form for \( x(r) \) has been assumed:

\[
x_i(r_i) = \sum_j c_j e^{\frac{r_i - r_{ij}}{b_j}}, \quad i = 1..n
\]  

(2.21)

For adsorption of an atom \( A \) on a metal surface, \( n \) corresponds to the coordination number (i.e. \( n = 2 \) for a bridge site, \( n = 3 \) for a threefold site etc.). The quantity \( x_i \) is referred to as the two body bond index. In general, the total bond index for multiple bonding is defined as

\[
X = \sum_i x_i(r_i) = N = 1
\]  

(2.22)

where normalisation to 1 is needed for \( a_2 \) to be the bonding energy of the two body interaction potential. Bond index conservation to unity has been verified by \textit{ab initio} calculations and allows evaluation of multi body quantities. For example, for a diatomic molecule like CO adsorbed in a bridge site with the carbon atom, the UBI
constraint is $x_{CO} + 2x_{Me} = 1$. Summarising the above information, the UBI-QEP model is based on four postulates:

i. the two body interaction potential is spherical and therefore only depends on the interbody distance;

ii. the two body interaction potential has a single minimum;

iii. the two body interaction potential is expressed as a polynomial function of an exponential variable, which is called the bond index;

iv. the multi body potential is obtained additively from the two body components with the constrain of the conservation of the total bond index.

On the basis of these points, several quantities can be calculated: atomic and molecular heats of adsorption, dissociation barriers, coverage dependence of the adsorption energies and so far. Here, only the results from the analytic formalism of the model will be reported: for further details see Ref. [53].

Atomic heats of adsorption $Q_{nA}$ can be calculated within the framework of this model. The total energy is the sum of the pair wise bond energies of the adatom $A$ to the $n$ metal atoms of the $n$-coordinated site:

$$E = \sum_{i=1}^{n} [Q_{1A}r_i^2 - 2x_{1A}(r_i)]$$

(2.23)

Under the constraint of unity bond index conservation, the Lagrangian function is

$$L = E - \alpha \left( \sum_{i=1}^{n} x_i(r_i) - 1 \right)$$

(2.24)

where $\alpha$ is the Lagrangian multiplier. By solving the Lagrangian multiplier problem by minimisation, the adsorption energy $Q_{nA}$ for an adatom $A$ in an $n$-fold coordinated site is given by

$$Q_{nA} = Q_{1A} \left( 2 - \frac{1}{n} \right)$$

(2.25)

where $Q_{1A}$ is the atomic adsorbate binding energy in the on-top site. This relation reflects a general trend where the adsorption energy increases with coordination (atomic carbon, oxygen, hydrogen ...) , but one should beware that it does not hold
for specific cases like carbon monoxide, which generally prefers low coordinated sites
(on-top and bridge). The application of this model must therefore be done with care,
depending on the cases. In a similar way, also the atomic heat of adsorption can be
obtained as a function of the local surface coverage by applying the conservation of
the bond index. For an adsorbate atom $A$ in an $n$-fold site one obtains

$$Q_{nA}(\theta) = Q_{nA} \left[ \frac{1}{n} \sum_{i} \frac{k_i}{m_i} \left( 2 - \frac{1}{m_i} \right) \right]$$

(2.26)

where $k_i$ is the number of surface metal atoms of type $i$ bound to $m_i$ adsorbates and
$Q_{nA}$ is the zero coverage limit binding energy in the $n$-coordinated site.

Analogously, molecules can also be treated. For a diatomic molecule $AB$, there
are three types of molecule-surface interactions considered by the model: weak,
medium and strong binding. Weak binding occurs for closed-shell molecules (e.g. CO,
$\text{N}_2$, $\text{H}_2\text{O}$, $\text{NH}_3$, $\text{CH}_3\text{CO}$) or molecules with strongly delocalised unpaired electrons (e.g.
$\text{O}_2$, NO); in this case, if the molecule adsorbs via the $A$ atom in an $n$-fold site, the
adsorption energy is given by

$$Q_{n,AB} = \frac{Q_{nA}^2}{Q_{nA} + D_{AB}}$$

(2.27)

where $D_{AB}$ is the gas phase dissociation energy of the molecule, which in this case is
equal to the bond energy. The dissociation energy is indeed defined as the energy
necessary to cleave a bond to give the constituent radicals ($D_{H,O \rightarrow OH+H} \neq D_{OH \rightarrow O+H}$),
while the bond energy is the average of the dissociation energies ($E_{H,O} = 0.5 \times \{D_{H,O \rightarrow OH+H} + D_{OH \rightarrow O+H}\}$) [60]. Strong binding occurs for molecular
radicals with localised electrons such as OH, CH and CH$_3$O: in this case, the
adsorption energy is given by

$$Q_{n,AB} = \frac{Q_{nA}^2}{Q_{nA} + D_{AB}}$$

(2.28)
In the medium binding condition, valid for monovalent radicals like the methyl group, the binding energy is calculated as the average of the previous two. Polyatomic molecules are treated as an extension of the diatomic case: if \( A \) is the atom which binds to the surface, \( B \) is defined as the rest of the molecule; for mono-coordination the equations remain the same as for the diatomic case. For asymmetric di-coordination of a chelated molecule \( A-X-B \) which binds to the surface with both \( A \) and \( B \) atoms to on-top sites, the total binding energy is given by

\[
Q_{AXB} = Q_{AX} + Q_{BX} - \frac{Q_{1AX}Q_{1BX}}{Q_{1AX} + Q_{1BX}}
\]  

(2.29)

Within the framework of the model also dissociation can be considered, thus obtaining estimates for the decomposition barriers on a surface. For the dissociation of an \( AB \) molecule to \( A \) and \( B \) fragments, the enthalpy change \( \Delta H \) is

\[
\Delta H = D_{AB} + Q_{AB} - Q_A - Q_B
\]  

(2.30)

and the reaction barrier \( \Delta E_{AB} \) is evaluated by

\[
\Delta E_{AB} = \frac{1}{2} \left( \Delta H + \frac{Q_A Q_B}{Q_A + Q_B} \right)
\]  

(2.31)

Within the model, \( \Delta E_{AB} \) is simply obtained from the energy of the intersection of the two potential energy curves (the one of the parent molecule and the one of the decomposition products). The UBI-QEP model, despite its simplicity, has been successfully used in several cases to estimate adsorption and reaction energies [53]. However, because of its simple underlying assumptions, care has to be taken in accepting the values of the estimated parameters: as an example, for methanol adsorption on metal surfaces [61] the model predicts that the first bond to break is a C-H bond, while there is experimental evidence for the dissociation of the O-H bond [62] to form adsorbed methoxy species. The results that are obtained by the application of the UBI-QEP model should be therefore considered only as a fingerprint: it is clear that the best calculation accuracy can be obtained only within the DFT framework.
2.3.2 A benchmark: ethanol decomposition on Pt(111)

Ethanol (CH₃CH₂OH) decomposition on Pt(111) was studied with the UBI-QEP model for providing a benchmark. This system has been chosen in relation to the work which will be presented in Section 4.1. Decomposition of EtOH on this metal surface has already been studied and further insight into the de-hydrogenation mechanism has recently been obtained with the aid of surface science techniques. Therefore, a direct term of comparison was already available in the literature [63,64]. Indeed, both computational approaches within the framework of DFT [63] and experimental spectroscopic measurements [64] have been employed to study the reaction on a model Pt(111) single crystal surface.

Adsorption energies, dehydrogenation barriers and activation energies for C-C, C-O, C-H and O-H bond cleavage in reaction intermediates have been evaluated with the model. The input data for the calculations have been obtained from the literature. Atomic heats of adsorption, molecular adsorption geometries and intramolecular bond energies have indeed been supplied by both experimental and DFT data [60,61,63,65-67].

Heats of adsorption of the possible reaction intermediates for ethanol decomposition on Pt(111) have been evaluated with the UBI-QEP model for direct comparison to the values computed with DFT methods in [63]. The results are summarised in Figure 2.11. It can be observed that the general trend is qualitatively reproduced on the eV scale with few exceptions. Best results are obtained when the UBI-QEP model is applied only once. As an example, the adsorption energies for acetaldehyde (CH₃CHO) and hydroxyethylene (CH₂CHOH) can be compared. In the former case, the molecule is doubly coordinated and binds to the metal surface via its oxygen and carbon atoms in an on-top configuration. In this case, the atomic binding energies in the on-top sites are evaluated from the hollow site values and in a second step the molecular heat of adsorption is calculated. The model is therefore applied twice. A UBI-QEP value for the binding energy of 0.34 eV is obtained, to be compared to the DFT value of 0.18 eV [63]. In the case of hydroxyethylene, on the contrary, which binds to the metal via the carbon atoms, atomic binding energies in the right adsorption sites are already available in the literature [68,69]. Indeed, the value of 0.94 eV is perfectly reproduced [63].
In general, it has been observed that the input data are of core importance. When considering DFT calculations, for example, it is well known that relative energy differences within the same work are obtained with great accuracy. On the contrary, absolute values can differ substantially from one framework to the other. Therefore, when more than one source is used for the input parameters of a UBI-QEP calculation, care has to be taken because errors are then propagated and amplified through the whole calculation. As an example, the CO heat of adsorption is available both from the experiment and from DFT calculations. Values of 1.43 [68] and up to 2.12 eV [70] have been reported respectively. It is clear that initial errors of 50% can dramatically affect the whole UBI-QEP calculation.

A clear correlation between the error on the calculated heats of adsorption and the bond lengths has been observed. In Figure 2.12, UBI-QEP adsorption energies for mono-coordinated intermediates have been plotted as a function of the bond distance calculated by DFT methods in [63]. Data have been fitted with an exponential function.
to guide the eye. It is evident that the shorter the equilibrium distance, the bigger is the error (in defect) due to the model. This can be tentatively explained by referring to the bond index definition which is at the basis of the whole UBI-QEP model. Bond indexes are defined as polynomial functions of exponentials, under the assumption that atomic functions' radial parts show this profile (see Equation 2.21). This is indeed true for high distances from the core, while, at short bond lengths, overlap of charge densities with profiles which deviate from an exponential shape occurs. Generally, it can be concluded that the UBI-QEP model underestimates binding energies for bond lengths which are shorter than 2.0-2.5 Å.

Figure 2.12 - Error in the calculated heats of adsorption as obtained from the UBI-QEP model with respect to values from DFT in [63]. Data for mono-coordinated molecules have been plotted as a function of the bond length [63] to the metal atoms. Fitting with an exponential function has been plotted in the graph to guide the eye.

C-C and C-O bond cleavage

C-C and C-O dissociation energies for the most stable reaction intermediates have been evaluated within the DFT framework in [63]. The most favourable intermediate for C-O bond scission is found to be 1-hydroxyethylidene (CH$_3$COH). The UBI-QEP model identifies, in addition to CH$_3$COH, also another candidate,
hydroxyethylene (CH₂CHOH) with the same activation barrier. For the decarbonilation reaction, DFT calculations show that the ketenyl intermediate (CHCO) has the lowest dissociation energy. This is true also for the UBI-QEP model only if we exclude C-C bond scission in acetaldehyde, which is found to have the lowest dissociation barrier in contrast with the DFT results.

It has to be observed that reference DFT values for the barriers in [63] are excessively high. As an example, C-C bond cleavage activation energies for ketenyl and ketene are found to be 0.95 and 1.34 eV respectively. This would imply that, assuming a standard pre-exponential factor of $10^{13}$ s$^{-1}$, bond scission occurs at temperatures higher than 440 K, in contrast with the experiment [64], where CH$_x$ species and CO are observed already below 200 K. On the contrary, with the UBI-QEP model, decomposition barriers of 0.26 and 0.22 eV are obtained for the two species respectively, thus properly reproducing the experimental data (see Figure 2.14).

**Intermediate dehydrogenation and simulation of the whole decomposition reaction**

Dehydrogenation barriers for the considered possible intermediates have also been calculated with the UBI-QEP model. These values were not computed in the DFT work [63], even if the competition between dehydrogenation and C-C/C-O scissions actually determines the real reaction path. A possible complete dissociation path is instead proposed in [64] on the basis of spectroscopic data. The following reaction path was obtained by simple application of the model, when only dehydrogenation reactions were considered.

\[
CH_3CH_2OH \xrightarrow{0.52 eV} CH_3CHOH \xrightarrow{\text{not stable}} CH_3CHO \xrightarrow{0.13 eV} CH_3CO \xrightarrow{0.29 eV} \\
CH_2CO \xrightarrow{0.70 eV} CHCO \xrightarrow{0.50 eV} CO
\]  

(2.32)

At this point, it was therefore tempting to simulate the whole EtOH decomposition reaction including also the C-C scission, thus determining the complete UBI-QEP path. Decarbonilation of the ketenyl intermediate as well as of acetyl (CH$_3$CO) were both included in the reaction on the basis of the experimental results in [64]. In [64], CH$_3$CO is proposed as a stable intermediate from analogies with acetaldehyde decomposition on the same surface, while the ketenyl is the favourable configuration for C-C cleavage. From the model calculation, similar decarbonilation barriers are obtained for the two species (0.26 and 0.22 eV respectively). The final reaction path as obtained from the model contains therefore two parallel decomposition mechanisms.
2. Experimental and computational background

\[ CH_3CO \rightarrow CHCO \rightarrow CH + CO \]  \hspace{1cm} (2.33)

\[ CH_3CH_2OH \rightarrow CH_3CHO \rightarrow CH_3CO \rightarrow CH_2 + CO \rightarrow CH + CO \]

Rate equations have been written for the reaction 2.33. Three processes have been considered, depending on the intermediates: first order desorption (Eq. 2.34), recombinative second order desorption (Eq. 2.35) and dissociation (Eq. 2.36).

\[ \frac{d\theta_{CO}}{dt} = -v_0 \theta_{CO} e^{-\frac{E_{DA}}{k_B T}} \] \hspace{1cm} (2.34)

\[ \frac{d\theta_H}{dt} = -2v_0 \theta_H^2 e^{-\frac{E_{DA}}{k_B T}} \] \hspace{1cm} (2.35)

\[ \begin{cases} \frac{d\theta_{AB}}{dt} = -v_0 \theta_A \theta_B e^{-\frac{E_{DA}}{k_B T}} \\ \frac{d\theta_A}{dt} = +v_0 \theta_A \theta_B e^{-\frac{E_{DA}}{k_B T}} \\ \frac{d\theta_B}{dt} = +v_0 \theta_A \theta_B e^{-\frac{E_{DA}}{k_B T}} \end{cases} \] \hspace{1cm} (2.36)

A standard pre-exponential factor \( v_0 \) of 10^{13} \, s^{-1} has been assumed for all surface reactions. A linear temperature ramp of 0.4 K/s has been used for the integration of the rate equations, in analogy with the XPS experiment [64]. Desorption curves for H2, CO and EtOH are plotted Figure 2.13 b. Ethanol desorption is remarkably well reproduced by the model. It can be observed that two main desorption states are present for hydrogen: the peak at lower temperature is desorption limited and due to the first dehydrogenation steps of the ethanol molecule. The feature at about 400 K is correlated to the CHx decomposition. There is clear qualitative agreement with the experiment. Carbon monoxide is instead only desorption limited. The mass 28 peak position depends therefore only on the desorption energy value. CH4 desorption as detected in the TPD experiments (see Figure 2.12 a) and was explained by subsequent re-hydrogenation of the CH groups [64]. This reaction was not included in the simulation and will be discussed here below.
2. Experimental and computational background

Figure 2.13 - Experimental TPD spectra (a) from [64] and results from the simulation based on the UBI-QEP model (b) for ethanol decomposition on Pt(111).

In Figure 2.14, both experimental (a) and computed (b) surface species concentrations are plotted for direct comparison. For the UBI-QEP calculation, the signal of the ethanol which undergoes decomposition is reported, while EtOH desorption is considered for the TPD experiment only. The CH₃ and CH trends are well reproduced. Carbon monoxide desorption occurs at lower temperature in the experiment, probably due to lateral interaction effects: model calculations were indeed
performed in the zero-coverage limit. With the UBI-QEP model, an ethanol dehydrogenation barrier of 0.52 eV and a binding energy of 0.44 eV are found.

![Graph showing reaction simulation results.](image)

**Figure 2.14** - Experimental (a) data from a high resolution fast XPS experiment of ethanol decomposition on Pt(111) [64] to be compared with the curves (b) as obtained by reaction simulation with the simple UBI-QEP model. See text for details.

Acetyl (CH$_3$CO) most likely dissociates via C-C bond cleavage (0.26 eV), rather than dehydrogenating (0.29 eV). Indeed, only about 20% of the ethanol molecules decompose through the stable ketene intermediate (CH$_2$CO) and subsequently decompose via ketenyl (CHCO) to CH and CO. This picture would explain the CH$_4$ desorption peak observed experimentally [64]. The authors in [64] candidate CH$_3$CO as a stable intermediate, while they suggest that C-C cleavage occurs in the ketenyl. This would imply that CH$_4$ is formed by multiple
hydrogenation of CH groups, rather than from the CH$_3$ + H reaction. By CH$_3$ adsorption on a D precovered Pt(111) surface, it was shown [71] that exchange reactions can occur. It was proven that two competitive mechanisms are present: i) CH$_3$ dehydrogenation to surface carbon and hydrogen; ii) CH$_3$ re-hydrogenation to methane. However, in the TPD experiments only CH$_3$D species were detected, thus indicating that CH$_x$ groups with $x=1,2$ further decompose, rather than hydrogenate. The picture suggested by the UBI-QEP calculation is compatible with both the DFT and experimental works: the proposed reaction mechanism leads in fact to the formation of CH$_3$ and CH groups on the surface by distinct parallel reaction paths. In a second step, methyl groups can both re-hydrogenate to methane, thus explaining the mass 14 peak observed in the TPD measurements, or dissociate to carbon and hydrogen. The proposed stable intermediate is CH$_2$CO, which is not in contrast with the spectroscopic data, where CH$_3$CO was only tentatively proposed.

Conclusions

By means of the simulation of ethanol decomposition on Pt(111), a benchmark for the UBI-QEP model has been obtained. It has been shown that also quantitative agreement can be obtained when calculating zero coverage heats of adsorption and reaction barriers. A correlation between errors in the calculated binding energies and the bond lengths has been found. It was also shown that care has to be taken when choosing the input values, depending on the source, due to differences in absolute values (within DFT frameworks) and discrepancies with experimental values. Calculated C-C and C-O decomposition barriers are not in line with data from DFT calculations [63]. The model predicts for example C-C cleavage in acetaldehyde, which is not the case. However, other intermediates fit better and for example agreement is found on ketenyl decarbonilation. As already observed, it has to be mentioned that DFT values predicted in [63] are definitely too high, while reaction barriers for C-C scission obtained with the model are in line with the experiment [64]. The model well reproduces dehydrogenation barriers, as can be seen form the complete reaction simulation.

Within the present benchmark for the UBI-QEP model, DFT results have been considered as a reference. However, it is known that *ab initio* calculations can fail in the treatment of some interactions, yielding under- or over-estimation of the associated energies. Discrepancies between results from the two frameworks are therefore not necessarily indicating a failure of the simple model, even if DFT methods are with no doubt the most reliable *ab initio* resources at present. On the basis of these considerations, data plotted in Figure 2.11 seem to show that DFT values for
strong interaction energies (above 1 eV) are generally higher than UBI-QEP values, while weak interactions are underestimated by DFT with respect to the model. For this reason, comparison to the experiment has also been considered in order to obtain a complete picture of the system. On the basis of the present analysis, it is concluded that the UBI-QEP model can be used for qualitative estimations of reaction energies. However, care has to be taken on the results and close comparison has to be carried out with experiments and \textit{ab initio} work where available. Finally, critical dependence on the input parameters has been demonstrated.
3. Molecular and atomic hydrogen interaction with single crystal metal surfaces

3.1 Coverage-dependent H adsorption site determination on Rh(100) by means of high-resolution core-level spectroscopy

It is shown that high-resolution real-time X-Ray Photoelectron Spectroscopy can be used to determine hydrogen adsorption sites as a function of coverage on Rh(100). The measurement of the surface core level shifts does not suffer from the lack of direct sensitivity of other surface probes due to the low scattering cross section and high mobility of atomic hydrogen. At low temperature (70–140 K) and coverage (below 0.25 ML), it is found that hydrogen adsorbs on Rh(100) in fourfold hollow sites, while at higher coverage bridge sites are preferred. By comparing the experimental spectra with the results obtained from Monte Carlo simulations, each surface component of the Rh 3d_{5/2} core level is associated with a specific adsorption configuration. A value of 0.74±0.08 for the hydrogen initial sticking coefficient is obtained, in very good agreement with previous reports.
3. Molecular and atomic hydrogen interaction with single crystal metal surfaces

3.1.1 Introduction

The understanding of the hydrogen-metal interaction at a fundamental level is of primary relevance, since there is a great technological interest in the behavior of metal surfaces in the presence of hydrogen. As a clean energy vector, hydrogen is regarded as one of the most promising solutions to the environmental impact of the growing energy demand [72-74]. Progress in the understanding of the interaction of hydrogen with metals is a fundamental step for the definition of the properties of materials needed for hydrogen production [75], storage [76] and final burning in fuel cells [74].

The dissociative chemisorption of hydrogen on single crystal metal surfaces has been widely studied by means of both theoretical and experimental techniques [1,4,32]. The trouble in the latter case is the limited sensitivity of conventional surface probes to the low scattering cross section of hydrogen atoms adsorbed on solid surfaces [32,77]. Nevertheless, in specific cases, Low Energy Electron Diffraction, Surface X-Ray Diffraction, He Scattering, Ion Scattering and High Resolution Electron Energy Loss Spectroscopy have been successfully applied for the determination of the hydrogen adsorption sites [32]. Recently it has been shown that STM images can be misleading [33]: the tip influences and actually drags the adsorbed hydrogen atoms into the bridge sites, showing a larger apparent adsorbate coverage (2 ML) (Figure 3.1).

On Rh(100), dissociative hydrogen chemisorption has been extensively studied with conventional surface science probes [2,5,6,16,33,39,78-80,]. Desorption spectra after hydrogen saturation at 95 K show two peaks [78]: the most prominent at 330 K and an additional high coverage feature at 130 K. A desorption energy of 1.05 eV is found, which is almost constant up to about 0.8 ML, drastically decreasing for higher coverage. At saturation (0.9 ML), HREELS spectra [78] show a prominent feature at 82 meV which is attributed to the perpendicular stretching mode for H adsorbed in the hollow site. A second feature, at 152 meV, is interpreted as the first overtone of the 82 meV vibration; a third, only partially resolved loss at 138 meV, is not clearly understood. At lower coverage (0.4 ML) only one feature is present at 70 meV. More recent higher energy resolution EELS measurements [79] show that at intermediate coverage the spectra consist of a superposition of low-coverage losses and saturation (1.0 ML) losses. In particular, high-coverage features show up in the vibrational spectra already at 0.56 ML. Early DFT calculations [39,80] state that the adsorption energy difference between hollow and bridge sites for hydrogen on Rh(100) is 170 meV at 1 ML (neglecting zero point energies, which are of the order of 120 meV).
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Figure 3.1 - Room-temperature STM images (50 x 50 Å²) of the same area of a Rh(100) surface after exposure to 15 L of H₂ at (a) 0.5 mV, 4 nA and (b) 0.5 mV, 9 nA. Using the various defects and impurities as markers, one can easily determine that the protrusions in (b) are in bridge sites [33].
More recent DFT results [6] point out that the determination of the saturation coverage is non-trivial since the energy difference between possible adsorption sites is too small with respect to the calculation accuracy. It is found that repulsive lateral interactions between adsorbed atoms are reduced in islands of high coverage (up to 2 ML), bridge-bonded hydrogen. Most recent DFT calculations [2,5] lead to the conclusion that, with the inclusion of the relativistic effects, the computed energy difference between the two competing adsorption sites is reduced to 40 meV, so that even zero point energy differences could become relevant in determining the preferred adsorption site. Experimentally, a quantitative LEED analysis [33] reports a saturation coverage of 1.1±0.6 ML at 120 K, with about 0.9 ML of hydrogen atoms in hollow sites and the remaining adsorbed in bridge positions, while accurate TPD measurements yield a saturation coverage of 1.22 ML [16,33]. In summary, divergences exist in the literature about the adsorption site and the saturation coverage of hydrogen on Rh(100), reflecting the experimental and theoretical difficulties described above.

In this section I will show how the analysis of the hydrogen-induced Rh 3d5/2 surface core level shifts provides a clear insight into the coverage-dependence of the adsorption site for hydrogen on the Rh(100) surface. For the analysis, the adsorbate-induced Surface Core Level Shifts (SCLS) model recently proposed [81] has been successfully applied. The results are complemented by Monte Carlo simulations based on the Unity Bond Index - Quadratic Exponent Potential model [52,53] described in Section 2.3.

3.1.2 Experimental and theoretical background

High resolution real-time X-Ray Photoelectron Spectroscopy experiments have been carried out at the SuperESCA beamline [41,42,82-85] of ELETTRA, which has already been described in the previous chapter. The sample was cooled by liquid nitrogen and heated by electron bombardment from a hot tungsten filament. It was cleaned following standard procedures by repeated Ar+ sputtering cycles, annealing to 1300 K, oxygen treatments and a final hydrogen reduction. Surface cleanliness was checked by measuring the C 1s and O 1s XPS signals, as well as by comparing the Rh 3d5/2 SCLS value for the clean surface with those reported in the literature [86-89]. The hydrogen doses are expressed in Langmuir (1 L = 10^-6 torr s) and are corrected for the ion gauge sensitivity factor.

The different surface core level shifted components of the 3d5/2 experimental spectra are attributed to surface Rh atoms differently coordinated to hydrogen atoms,
following a model recently proposed [81]. In this model a clear dependence of the shift of the surface component on the local adsorption structure is demonstrated on the basis of both experimental data analysis and DFT calculations. This behavior is determined by initial state effects related to the electronic environment of the system [90]. Final state contributions, which originate from the core hole screening, need to be considered for a precise and quantitative characterization of SCLS values [91]. However, both experimental and DFT calculations have shown that for Rh(100) initial state effects dominate [81,89]. In the present study, this assumption is therefore used. Within the framework of this model, the energy shift $\Delta E_{ij}$ (with respect to the position of the clean surface component) of the Surface Core Level of a substrate atom bound to $i$ atoms adsorbed in $j$-fold site symmetry, can be expressed as

$$\Delta E_{ij} = i \times \Delta E_{i,1}$$ (3.1)

This shows the additivity of the energy shift of a core level, which is caused by the single contributions of different "fractions" of adsorbate atoms. Similarly, a metal atom bound to an adsorbate with coordination number $j$ displays a shift given by

$$\Delta E_{i,j} = \frac{1}{j} \times \Delta E_{i,1}$$ (3.2)

The Rh 3d$_{5/2}$ core level spectra have been fitted, after linear background subtraction, with Doniach-Sunjic line shapes convoluted with a Gaussian function [92]. The former is described by two parameters, the Anderson singularity index $\alpha$, correlated to the final state screening, and the Lorentzian width $\Gamma$, which depends on the core hole lifetime [86,92]. In the fitting procedure, the $\alpha$ and $\Gamma$ parameters for the bulk, first and second layer peaks were initially fixed at the values previously found for the same surface [86]. The Gaussian contribution was allowed to vary in the least square fitting procedure, since its value depends on the energy resolution, surface temperature and surface inhomogeneity. In a second step, for each experimental condition (i.e. photon energy, energy-resolution and photoelectron emission angles), all the fitting parameters were released for the clean surface spectra, yielding the "best fit" values, which were then used for deconvoluting the hydrogen uptake and desorption data.

In order to describe the evolution of the surface layer during the hydrogen uptake and link them to the behavior of the observed core level components, Monte Carlo simulations were performed, within the framework of the UBI-QEP model [52,53]. As already shown (Chapter 2), this model allows to evaluate the adsorption energy of atoms adsorbed on single crystal metal surfaces as a function of
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coordination, taking into account their indirect, substrate-mediated lateral interactions. The only input of the simulations is the adsorption energy of hydrogen on Rh(100) calculated by DFT in the zero coverage limit [2,5,33]. Monte Carlo simulations have been performed on a (15×15) unit cell with periodic boundary conditions. The dimension of the unit cell was selected in order to minimize border effects and to allow reasonable computation times: even simulations performed on (10×10) and (12×12) cells did not show substantial differences. For each selected surface coverage \( \theta_n \), the hydrogen uptake was performed randomly with no discrimination between the fourfold and bridge adsorption sites. Equilibration of the system was always reached within 5000 Monte Carlo steps (mcs); in each of the mcs, \( \theta_n \times 15 \times 15 \) hydrogen atoms were randomly chosen, the hopping direction was randomly selected and finally the hopping probability was calculated for each of the selected adsorbate atoms. The site occupancy probability was calculated using the Boltzmann distribution, the adsorption energies for each local configuration were calculated using the UBI-QEP model and the hopping process was controlled by the Metropolis algorithm. Simulations have been carried out at final temperatures ranging from 60 to 200 K, using simulated annealing equilibration. No differences have been observed between single- or multiple-hopping kinetics, nor between independent or sequential uptakes (i.e. starting for each increasing coverage from the clean surface or adding extra hydrogen to the previous equilibrated configuration). The reliability of the code was checked by reproducing the results obtained by Hansen and co-workers [93] for oxygen adsorption on the Rh(100) surface up to 0.5 ML. Simulations for hydrogen were performed only up to a surface coverage of 0.6 ML, as the UBI-QEP model is known to fail at high concentrations, due to over-estimation of the adsorption and interaction energies [53].
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Figure 3.2 - Selected Rh 3d₅/₂ spectra collected during the hydrogen uptake at 140 K (hv=407 eV). The several contributions to the surface peak shape are shown. The binding energy scale is referred to the bulk component position. Bulk and second-layer components are not shown.
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3.1.3 Results and discussion

High resolution time-resolved XPS spectra of the Rh 3d5/2 core level were collected during hydrogen uptake at several temperatures between 70 and 140 K: no differences were detected within this range. For the clean surface (see Figure 3.2) three contributions have been identified and assigned to bulk, first- and second-layer atoms, respectively. The clean surface first-layer peak (R0) is positioned at -626±5 meV from the bulk peak (Rb). A second layer contribution, revealed also on Rh(111) [94], is centered at +75±10 meV, in agreement with previous findings [95]. The “best fit” parameter values are Γ1=0.23 eV and α1=0.27, Γ0=0.28 eV and α0=0.20, Γ2nd layer=0.19 eV and α2nd layer=0.10, for the bulk, first and second layer, respectively. Again these values are in good agreement with previously reported data [86].

During the hydrogen uptake, the clean surface Rh 3d5/2 component progressively vanishes, while new components grow at higher binding energies, closer to the bulk peak (see Figure 3.2). By least square fitting, three other surface related peaks are found, positioned at -547±5 meV (R1), -481±5 meV (R2) and -308±5 meV (R4) from the bulk peak, respectively. Alternatively, by referring their position to the clean surface peak, the new features are centered at Δ, 2Δ and 4Δ respectively, giving for Δ a value of 79±5 meV (see Figure 3.3).

![Figure 3.3 - Rh 3d5/2 peak positions with respect to the bulk component, associated to the non-equivalent surface rhodium species. The linear fit to obtain the value for the quantization of the SCLS displacement (Δ) is shown.](image)
Remarkably, the “3Δ” SCLS component is absent from the spectra; even forcing a peak at this position, its intensity goes to zero during the fitting procedure. Using the SCLS model [81], the different surface components can be attributed to specific bonding geometries: in particular, the peak R1 centered at $\Delta=\Delta E_{1,4}$ can be associated to surface rhodium atoms bound to a single hydrogen atom adsorbed in a fourfold site. Analogously, the peak R2 at $2\Delta=\Delta E_{2,4}=\Delta E_{1,2}$ can be attributed to rhodium atoms bound to two hydrogen atoms in fourfold sites or, equivalently, to rhodium atoms bonded to single hydrogen atoms in bridge sites. Finally, the feature $R_4$ at $4\Delta=\Delta E_{4,4}=\Delta E_{2,2}$ corresponds to surface atoms bound to four hydrogen atoms in hollow sites or to rhodium atoms bound to two hydrogen atoms in bridge positions (see Figure 3.4).

**Figure 3.4 - Surface model showing the classification of the non-equivalent first layer rhodium atom species: $\Delta=\Delta E_{1,4}$, $2\Delta=\Delta E_{2,4}=\Delta E_{1,2}$, $4\Delta=\Delta E_{4,4}=\Delta E_{2,2}$.**

Analyzing the behavior of the peak intensities as a function of the hydrogen exposure (see Figure 3.5), it can be observed that the contribution of $R_4$ vanishes at about 0.2 L, but grows back again around 0.5 L. As previously reported [79], hydrogen saturation is reached at about 2 L; at this coverage only two surface first-layer components ($R_3$ and $R_4$) are present. During the whole uptake experiment the intensity of the $R_6$ component remains almost constant. Besides the hydrogen related components, a new second layer core level shifted component appears at $+48\pm10$ meV.
with respect to the bulk feature in the XPS spectra (see Figure 3.5). This component sets in above 0.1 L and grows up to saturation at the expenses of the clean surface second layer contribution centred at +75±10 meV, which vanishes at saturation. A similar behaviour for the second layer component has already been reported for hydrogen adsorption on W(100) [96], where a hydrogen-induced restructuring was involved.

![Figure 3.5](image)

**Figure 3.5 - Intensities of the Rh 3d_{5/2} surface and second-layer core level components as a function of hydrogen exposure at 120 K (hν=407 eV). The first-layer features are associated to the non-equivalent surface rhodium species: R₅ - clean surface; R₁ - Δ; R₂ - 2Δ; R₄ - 4Δ.**

At the end of each hydrogen uptake experiment, a desorption experiment was performed by annealing the sample to a specific temperature with a rate of 5 K/s, following immediate cooling to 150 K and collecting the XPS spectra.

In Figure 3.6 the behavior of the multiple core level shift components of the Rh 3d_{5/2} peak are reported as a function of the annealing temperature. The relative intensities of the surface components during desorption show the reverse behavior with respect to the uptake. In Figure 3.7, the derivative of the normalized sum of the intensities of the different contributions to the SCL peak is shown as a function of the annealing temperature, thus reproducing the hydrogen desorption rate.
Figure 3.6 - Intensities of the Rh 3d$_{5/2}$ surface and second-layer core level components as a function of the annealing temperature. All spectra were collected at a temperature of 120 K ($h\nu=407$ eV). The first-layer features are associated to the non-equivalent surface rhodium species: $R_S$ - clean surface; $R_1$ - Δ; $R_2$ - 2Δ; $R_4$ - 4Δ.

Figure 3.7 - Derivative of the normalized sum of the intensities of the different contributions to the SCL peak as a function of the annealing temperature, thus reproducing the hydrogen desorption rate.
Figure 3.8 - Selected structural models of the equilibrium configurations obtained by Monte Carlo simulations during hydrogen uptake. Unit cell dimensions: 15×15; final simulation temperature: 120 K; nmcs: 5000.
Monte Carlo simulations for increasing hydrogen coverage (in the 0.0-0.6 ML range with 0.025 ML steps) at 120 K have been performed. An adsorption energy difference between hollow and bridge sites of 40 meV and an adsorption energy of 2850 meV (QA) [97] for the zero-coverage limit in the fourfold site were assumed [2,5,33]. In Figure 3.8 the instantaneous configurations obtained after equilibration for selected adsorbate coverages are reported. At 0.25 ML almost all adsorbed atoms are in fourfold hollow sites. The small difference in the heat of adsorption between bridge and hollow sites allows occasional occupation of the bridge sites, which decreases when the surface temperature in the simulations is lowered. Accordingly, the surface rhodium atoms are mainly of "Δ" type (see Figure 3.4). As the hydrogen coverage increases, the lateral interactions progressively make more energetically convenient to populate bridge sites. During this process, "2Δ" rhodium atoms become predominant (as can be seen in Figure 3.8 for the 0.35 ML surface), while some surface atoms remain free from adsorbed hydrogen atoms. This effect accounts remarkably well for the growth of the R Peak at 0.5 L during the uptake (see Figure 3.5). At coverage higher than 0.5 ML (see Figure 3.8), all hydrogen atoms are in bridge sites, which gives rise to "2Δ" Rh atoms and, at the highest examined coverage (0.6 ML), also to "4Δ" surface atoms (i.e. atoms which are bonded to two adsorbate atoms in bridge sites). In agreement with the experiments, none of the simulations show the presence of "3Δ" atoms, which require higher values of the adsorption energy difference between the bridge and hollow sites (>80 meV).

The relative SCLS intensity for each surface configuration is simply assumed to be proportional to the population of each Rh surface species. By considering only metal atoms in the topmost layer and on the basis of the poor scattering properties of hydrogen, photoelectron diffraction effects can indeed be reasonably neglected at this stage and results from such a simple atom counting algorithm can be directly compared to the experiment. The final values for each equilibrated system, obtained upon averaging over the last 500 mcs of each simulation, are reported in Figure 3.9, bottom panel.

From data analysis it is clear that no "3Δ" Rh atoms are ever generated during the uptake and that two nonequivalent Rh surface atoms are present at saturation: at coverage lower than 0.25 ML only fourfold hollow sites are occupied, while for higher coverage hydrogen preferentially adsorbs in bridge sites. It is remarkable to compare the results of the SCLS analysis with the output of the Monte Carlo simulations. They both yield the hydrogen adsorption site population, but the former as a function of the hydrogen exposure, while the latter related to the surface coverage.

Assuming a second order process, the adsorption rate can be expressed as


\[ r = \frac{d\theta_H}{dt} = 2\frac{d\theta_H}{dt} = \frac{2p_{H_2}S_0\left(1 - \frac{\theta_H}{\theta_s}\right)^2}{\sqrt{2\pi m_{H_2}k_BT}} \]  

(3.3)

where \( p_{H_2} \) is the molecular hydrogen gas pressure, \( s_0 \) the initial sticking coefficient, \( \theta_s \) the surface saturation coverage, \( k_B \) the Boltzmann constant, and \( T \) the gas temperature. By integrating Equation 3.3, a direct relationship between surface coverage and exposure is obtained as a function of two unknown parameters only: \( s_0 \) and \( \theta_s \). A fitting procedure was performed, thus obtaining the values of \( s_0 \) and \( \theta_s \) which produce the best agreement between experiment and simulations. Figure 3.9 (top) shows the experimental data plotted vs coverage, which now can be directly compared with the results reported in Figure 3.9 (bottom), evidencing a remarkable agreement. All the features of the simulations are present in the experimental data, even the persisting intensity of the clean surface component above 0.3 ML, linked to the change in the adsorption site (from hollow to bridge).

Figure 3.9 - Comparison between experimental and simulation curves for the SCLS components as a function of surface coverage: \( R_5 \) - clean surface; \( R_1 - \Delta \); \( R_2 - 2\Delta \); \( R_4 - 4\Delta \).
From the fit, a value for $s_0$ of $0.74 \pm 0.08$ is obtained, in good agreement with the theoretical value of 0.8 [35] and with the recent experimental value of 0.85±0.15 [16]. Moreover, a saturation coverage limit of 0.80±0.07 ML is found: this is compatible with the value of 1.1±0.6 ML [33] and very close to the value of 0.9 ML reported in [78], while it is in contrast with the value of 1.22 ML determined by TPD calibration [16,33] (Figure 3.10).

**Figure 3.10** - Fitting of the experimental data after normalization to the simulation results; integration of Equation 3.3 yields a direct relationship between surface coverage and exposure, thus providing best fit values for $s_0$ and $\theta_0$. 
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3.2 Atomic hydrogen interaction with Ru(1010)

The interaction of atomic hydrogen with clean and deuterium pre-covered Ru(10\text{10}) was studied by means of TPD spectroscopy. Compared to molecular hydrogen experiments, after exposure of the clean surface to gas phase atomic hydrogen at 90 K, two additional peaks grow in the desorption spectra at 115 and 150 K. The surface saturation coverage, determined by equilibrium between abstraction and adsorption reactions, is 2.5 ML. Pre-adsorbed deuterium abstraction experiments with gas phase atomic hydrogen show that a pure Eley-Rideal mechanism is not involved in the process, while a Hot Atom (HA) kinetics well describes the reaction. By least square fitting of the experimental data, a simplified HA kinetic model yields an abstraction cross section value of 0.5±0.2 Å². By means of both TPD and XPS, atomic hydrogen interaction with the oxygen pre-covered surface was also studied: oxygen hydrogenation and water production take place already at very low temperature (90 K).

3.2.1 Introduction

As already discussed in Chapter 1, dissociative adsorption of hydrogen on transition metal surfaces can be an activated or a not activated process. In the former case, the energy required to overcome the dissociation barrier (about ten times higher than the average energy of gas phase H₂ at room temperature [3]) is balanced by the energy gained upon atomic adsorption. This first step can be eliminated and the overall reaction mechanism simplified by using atomic hydrogen beams, which can be produced with the aid of hot tungsten filaments [20], microwave discharge sources [44] or Bischler and Bertel sources [43,47].

Several experiments about atomic hydrogen interaction with single crystal metal surfaces have been carried out under UHV conditions [3,16,20,25,44-46,51,98,99]. The general trend is that H atoms i) produce a higher surface saturation coverage with respect to H₂ molecules [44-46]; ii) allow hydrogen adsorption on metals where hydrogen molecules do not dissociate (e.g. silver) [51,99]; iii) can overcome the diffusion barrier to the bulk, populating subsurface adsorption sites [3,16,20] and iv) show high reactivity towards the hydrogenation of hydrocarbons [3,20], small molecules [100-103] and single adatoms like oxygen [100].
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On Ru(10\(\bar{1}\)0), dissociative hydrogen adsorption has already been studied [7,104-106]. Several ordered structures form: a split (2\(\times\)2) at 1.0 ML, a (1\(\times\)2) at 1.2 ML, a c(2\(\times\)2) at 1.5 ML and a (1\(\times\)1)-2H phase at 2.0 ML coverage [104], where hydrogen populates threefold and/or bridge sites, depending on coverage and adsorption structure [7]. Atomic hydrogen interaction with this surface has not been studied yet. On the contrary, both molecular dissociative [107-113] and atomic [44-46] hydrogen adsorption have been studied on Ru(0001). It was shown that the way atomic hydrogen is produced affects the experimental results [44,45]: this is due to the differences in hydrogen atoms kinetic energy, source’s cracking efficiency, flux and possible presence of ions in the atomic beam. More specifically, when the atomic hydrogen was obtained by cracking on a hot tungsten filament, a saturation coverage of 1.42 ML was reached [45]; when instead a microwave discharge source was used, only 1.01 ML of hydrogen atoms could adsorb on the surface [44]. These values result from a steady-state balance between adsorption and abstraction and therefore clearly depend on the atomic hydrogen beam parameters. In the former case an Eley-Rideal first order mechanism was used to model the abstraction and adsorption reactions, successfully describing the experimental data. In the latter case, the absence of angular dependence of the abstraction cross section suggested a quasi-ER kinetics, better described by a Hot Atom precursor model [24,25]. This model was first proposed by J. Harris and B. Kasemo in [24], as already discussed in Chapter 2. There is controversial debate about the existence of transient mobility of adsorbed particles on solid surfaces and the role of this effect has been considered also for O\(_2\) dissociation [114].

3.2.2 Experimental setup

Experiments were carried out in the multi-purpose UHV experimental chamber (base pressure of 5\(\times\)10\(^{-11}\) mbar), which was described in Chapter 2. The sample was cooled down to 90 K by liquid nitrogen and heated up to 1300 K by resistive heating. For all TPD measurements, a linear temperature ramp of 2 K/s was applied to the sample.

The surface was cleaned by repeated Ar\(^+\) sputtering, annealing and oxygen treatment cycles, followed by final reduction with hydrogen at 1000 K, until a sharp (1\(\times\)1) LEED pattern was obtained. Absence of contaminants was checked by XPS. The cleaning procedure for the same surface had already been tested in a previous experiment by high resolution synchrotron radiation XPS [115]. Moreover, reproducibility of the hydrogen TPD spectra and direct comparison to data from the literature further assured the absence of contaminants [105]. In all XPS measurements a pass energy of 20 eV was used: the energy resolution was about 1 eV, being
dominated by the X-Ray source photon width. After linear background subtraction, spectra were fitted with Doniach-Sunjic line shapes [92] convoluted with a Gaussian function. Binding energies were calibrated with respect to the Ru 3d5/2 core level position at 280.0 eV.

Atomic hydrogen was produced using the home-made thermal cracker of the Bischler and Bertel type which is described in Chapter 2.

3.2.3 Results and discussion

Hydrogen uptake

In Figure 3.11, TPD spectra after exposure of the clean surface at 90 K to gas phase molecular hydrogen (right) and to the atomic hydrogen beam (left) are shown for increasing doses up to 25 L. In the former case, three peaks can be observed at 215 K (α), 250 (~α) and 340 (~3) respectively. The data are in agreement with a previously reported experiment [105], except from a small feature at 290 K (~3) which is not resolved in the present spectra. After adsorption of atomic hydrogen, two additional peaks grow at lower temperatures: a broad feature at 150 K (yz) and a sharp peak at 120 K (yt). In Figure 3.12, TPD spectra after surface saturation with molecular and atomic hydrogen at 90 K are superimposed for comparison; assuming a saturation coverage of 2.0 ML in the former case [105], a saturation coverage of 2.5 ML is obtained after the uptake with H atoms.

Deuterium abstraction

For the deuterium abstraction experiments, the clean surface was firstly saturated at 90 K with gas phase molecular deuterium. The layer was then exposed to the atomic hydrogen beam at the same temperature. Finally, a desorption experiment was performed. In Figure 3.13, H2, HD and D2 TPD spectra corresponding to different atomic hydrogen doses (up to 200 L) are shown. The quantity of D2 desorbing from the surface decreases as a function of the exposure to atomic hydrogen. In parallel, the low temperature peaks characteristic of atomic hydrogen exposure (~1 and ~2) appear also in the D2 and HD desorption spectra. After coverage calibration, an overall saturation coverage (H+D) of 2.5 ML is found. HD production reaches a maximum when the deuterium coverage equals the hydrogen coverage (1.25 ML). Moreover, for long exposures, where the final deuterium coverage is low (about 0.5 ML), substantial changes can be observed in the hydrogen desorption spectrum (top panel, curve (h)). The β1 peak becomes more intense; in parallel, γ2 grows higher than α and a new peak appears at 185 K. Longer atomic hydrogen exposures were not performed in order to
avoid surface contamination by residual background gases like carbon monoxide and water.

**Figure 3.11 - Hydrogen TPD spectra after exposure of the clean surface at 90 K to increasing doses (up to 25 L) of molecular (right) and atomic hydrogen (left).**
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Figure 3.12 - Comparison between mass 2 TPD spectra after saturation of the surface at 90 K with molecular (dashed curve) and atomic (solid curve) hydrogen.

Figure 3.13 - Mass 2, 3 and 4 TPD spectra after exposure at 90 K of the deuterium pre-saturated surface to increasing doses of atomic hydrogen. Atomic hydrogen doses are: a) 0.1 L - b) 1.2 L - c) 4.6 L - d) 12 L - e) 23 L - f) 46 L - g) 92 L - h) 185 L.
Oxygen reduction

Three different oxygen overlayers were prepared for the hydrogenation experiments at 90 K: a (2×1)pg (1 ML), a c(2×4) (0.5 ML) [116-118] and an intermediate coverage layer of 0.7 ML of oxygen. In Figure 3.14, hydrogen (left) and water (right) TPD spectra are shown, which were obtained after exposure of the oxygen layers to 25 L of molecular (top) and atomic (bottom) hydrogen.

Figure 3.14 - TPD spectra of hydrogen (left) and water (right) after exposure at 90 K of the oxygen pre-covered surface to 25 L of molecular (top) and atomic (bottom) hydrogen. Starting oxygen overlayers were (2×1)pg (1 ML), 0.7 ML and c(2×4) (0.5 ML).

Upon exposure to gas phase molecular hydrogen, only a small amount of water forms, most probably at surface defects; this quantity increases when increasing the initial oxygen coverage. A peak can be observed in the desorption spectra at 290 K on the c(2×4)-O, which shifts to 310 K in the 0.7 ML layer and moves to 380 K for the (2×1)pg-O. A second, smaller feature is present at 280 K on the 0.7 ML layer, shifting down to 260 K on the (2×1)pg-O structure. In the hydrogen desorption spectra, three peaks are visible at 125, 180 and 290 K respectively. The amount of desorbing hydrogen decreases as the initial oxygen coverage is raised.
On the contrary, when the oxygen pre-covered surface is exposed to gas phase hydrogen atoms, large amounts of water are produced: in the TPD spectra three water desorption peaks can be distinguished at 200, 240 and 295 K. Similarly to the previous case, the quantity of hydrogen desorbing from the surface decreases when the initial oxygen coverage is higher. After the hydrogen uptake on the ordered oxygen phases, only a (1×1) LEED pattern is observed.

Figure 3.15 - O 1s XPS spectra collected at 90 K in the oxygen hydrogenation experiment on two prepared overlayers with coverage of 0.7 (left) and 1 ML (right) respectively. 

XPS spectra of the O 1s core level were collected before and after the hydrogen uptakes on the (2×1)pg and 0.7 ML oxygen overlayers. After flashing the surface to the selected temperature, XPS spectra were always collected at 90 K. No changes in the O 1s peak were observed after exposure to molecular hydrogen. On the contrary, important changes are observed after exposure to atomic hydrogen, as shown in
Figure 3.15. In agreement with previous results [115], for the initial oxygen covered surfaces only one oxygen 1s peak is found at 529.9 and 529.8 eV, corresponding to 0.7 and 1.0 ML adsorbed oxygen, respectively. After atomic hydrogen uptake at 90 K, these peaks decrease in intensity and shift to higher binding energies (530.1 eV) in both cases. In parallel, a new feature grows at 532.5 and 532.7 eV, respectively. Upon annealing of the surface, these new peaks disappear in parallel with water desorption in the TDS spectra. At 270 K, a shift in their binding energy to 532.1 eV is observed. After the desorption experiments, the final surface shows a slight decrease in the oxygen coverage (20% in both cases) with respect to the initially prepared surfaces.

Figure 3.16 - O 1s XPS spectra collected at 90 K in the water adsorption experiment on the clean (left) and 1 ML oxygen pre-covered (right) surface.
For comparison, the XPS O 1s spectra were collected upon water adsorption (1 L) and desorption, both on the clean and oxygen pre-covered (1 ML) surfaces (see Figure 3.16). On the clean surface (Figure 3.16 - left), at 90 K two peaks grow: a more intense feature at 533.3 eV and a shoulder at lower binding energy (531.2 eV). The former decreases in intensity upon annealing and at 270 K is not visible anymore; the latter grows up to a maximum at 220 K, fades for higher temperatures but persists up to 470 K. On the contrary, only one additional peak at 532.4 eV is visible after water adsorption on the oxygen pre-covered surface (Figure 3.16 - right). In this latter case, similarly to what happens upon atomic hydrogen uptake on the oxygen covered surface, the O 1s peak due to atomic oxygen shifts to a higher binding energy by 0.2 eV (up to 530.0 eV). By annealing the surface, the species associated with the 532.4 eV peak desorbs. At 470 K, the initial oxygen layer is recovered on the surface, characterized by the same XPS intensity and position.

**Discussion: hydrogen uptake and deuterium abstraction mechanisms**

The mechanism of atomic hydrogen adsorption has been extensively discussed in the literature: in some cases a first order kinetics adequately fits the experimental data [44,45], but this is not always the case [25,98,100], depending also on the parameters of the atomic hydrogen beam.

In the present study on Rh(1010), a simple model is proposed, based on the HA kinetics, that adequately describes both the hydrogen adsorption and the deuterium abstraction processes.

In Figure 3.17, the uptake profiles obtained after integration and normalization of the hydrogen TPD spectra of Figure 3.11 are shown. The hydrogen dose is expressed in ML, assuming a surface density of 8.638×10^18 atoms/m² for Rh(1010) [104]. In the case of the molecular hydrogen uptake, a second order dissociative adsorption kinetics (Equation 3.4) has been adopted for the fit and a saturation coverage of 2 ML has been assumed to normalize the TPD integrals. The fitting procedure yields an initial sticking coefficient of 0.85±0.10 for the dissociative molecular adsorption process. In the case of atomic hydrogen uptake on the clean surface, different models have been tried: a first order kinetics (Equation 3.5 with n=1), a fractional order process with n>1 (Equation 3.5 with n>1) and a HA kinetics (Equation 3.6). The latter model best describes the experimental data: in this case, the fit has been performed simultaneously on three different sets of data (hydrogen uptake on the clean surface, hydrogen uptake on the deuterium pre-covered surface and deuterium abstraction), obtaining a unique best fitting parameter set.
Figure 3.17 - Molecular and atomic hydrogen uptake curves obtained from the TPD data shown in Figure 3.11 (markers), together with fits based on the kinetic models described in the text (lines). The inset provides a magnification of the initial part of the curves.

Figure 3.18 - Fitting of data obtained from the deuterium abstraction experiments with the HA model proposed in the text.
The data and fits for the latter two cases are shown in Figure 3.18, which was obtained by the TPD data of Figure 3.13, after correction for the mass spectrometer sensitivity factors [119].

In all the rate equations, \( s_0 \) is the initial sticking coefficient, \( \theta_S \) the hydrogen saturation coverage, \( \theta_H \) the actual hydrogen coverage on the surface. Equations 3.6, 3.7 and 3.8 describe the HA model for the hydrogen adsorption on the clean surface, hydrogen adsorption on the deuterium pre-covered surface and deuterium abstraction, respectively. Here \( \theta_H^* \) and \( \theta_S^* \) are the actual and saturation coverage of the HA species. In general, a complete HA kinetic description requires multiple contributions to the rate equations, leading to several free independent parameters in the fitting procedure [25,98]. To avoid this, two assumptions are made. Firstly, as previously done [25], it is assumed that the deuterium and hydrogen abstraction cross sections by a hot \( H \) atom are equal \((k_1=k_3)\). Secondly, it is assumed that \( \theta_H^*=\theta_S^*-\theta_D \), i.e. adsorbed hydrogen atoms directly reduce the HA saturation adsorption coverage. This latter assumption, for the case of deuterium abstraction, becomes \( \theta_H^*=\theta_S^*-\theta_H-\theta_D \).

\[
\frac{d\theta_H}{dt} = 2F_H s_0 \left( 1 - \frac{\theta}{\theta_S} \right)^2
\]
(Eq. 3.4)

\[
\frac{d\theta_H}{dt} = F_H s_0 \left( 1 - \frac{\theta}{\theta_S} \right)^n , \quad n \geq 1
\]
(Eq. 3.5)

\[
\frac{d\theta_H}{dt} = -k_1 \theta_H \theta_S^* + k_1 \left( 1 - \frac{\theta_H}{\theta_S} \right) \theta_S^* , \quad \theta_H^* = \theta_S^* - \theta_H
\]
(Eq. 3.6)

\[
\frac{d\theta_H}{dt} = -k_1 \theta_H \theta_S^* + k_2 \left( 1 - \frac{\theta_H + \theta_D}{\theta_S} \right) \theta_S^* , \quad \theta_H^* = \theta_S^* - \theta_H - \theta_D
\]
(Eq. 3.7)

\[
\frac{d\theta_D}{dt} = -k_3 \theta_D \theta_S^* , \quad k_3 = k_1
\]
(Eq. 3.8)

The fits shown in Figures 3.17 and 3.18 yield for the abstraction cross sections \( k_1 \) and \( k_3 \) the value of 0.5±0.2 Å², which is about half of what found for the same reaction on Ru(0001) [45], where atomic hydrogen was obtained using a hot tungsten filament. For the HA sticking \((H^* \rightarrow H_{ads})\) a much larger cross section \((k_2=3.3±0.4 Å²)\) is obtained, which can be expected by simple comparison of the total and the deuterium coverage curves in Figure 3.18: the surface reaches saturation after a dose of about 50 ML of H atoms, whereas, after 200 ML, more than 0.5 ML of deuterium
atoms are still present on the surface during the abstraction experiment. It was previously reported [25] that the kinetics of atomic hydrogen interaction with a selected metal surface (sticking vs hydrogenation) is controlled by the ratio between the adsorption and abstraction cross sections. This ratio, as obtained by Monte Carlo simulations compared to experimental data [25], is of the order of 100 for Pt(111), 10 for Ni(100) and 1 for Cu(111): for Ru(10\(\bar{1}\)0) \(\approx\) 3 is found here. Moreover, using the model proposed in this work, an ideal hydrogen saturation coverage (\(\theta_s\)) of 4±2 ML is obtained, indicating that the measured coverage of 2.5 ML is due to equilibrium between adsorption and abstraction. Finally, the found saturation coverage for the hot hydrogen species is \(\theta_s^*\approx2.6\pm0.4\).

**Discussion:** the process of oxygen hydrogenation

Pre-adsorbed oxygen hydrogenation by gas phase H atoms, generated by a Bischler and Bertel type source, has already been studied on Ni(100) [100]. An Eley-Rideal mechanism was proposed, where impinging hydrogen atoms directly react with adsorbed oxygen to form OH groups, with a cross section of 0.3 \(\text{Å}^2\). This is the rate limiting step for water formation, since the cross section for OH hydrogenation to water is much larger, 4.5 \(\text{Å}^2\). On ruthenium, water adsorption has been studied both theoretically and experimentally for the (0001) surface. Very recently, Feibelman [120] has proposed that, upon water adsorption, a partially dissociated layer grows, where both water molecules and hydroxyl groups are present, in agreement with previous XPS studies [121].

The results presented here can be explained using a similar picture: in the O 1s spectra, the peak at 533.3 eV is due to adsorbed water, while the shoulder at 531.2 eV is attributed to hydroxyl groups in the partially dissociated water overlayer. It can be noticed that the latter feature persist in the XPS experiment up to 470 K (Figure 3.16). While the main water desorption peaks are situated below 400 K in the TPD curves (Figure 3.14), there is indeed a long desorption tail up to 450 K which accounts for the presence of residual OH on the surface up to this temperature. Moreover, the sample was quickly flashed in the XPS experiments, while a gentle temperature ramp (2 K/s) was adopted in the TPD measurements: this accounts for the slight temperature difference. On the contrary, when the water uptake is performed on the oxygen pre-covered surface, only one peak is observed at intermediate binding energy (532.4 eV) in the XPS experiments. This is very close to the peaks growing when the oxygen overlayer is exposed to atomic hydrogen, at 532.5 and 532.7 eV for the 0.7 and 1.0 ML oxygen structures, respectively. On Ru(0001), it was found that water does not dissociate upon adsorption on the oxygen pre-covered surface [122]. It is therefore
3. Molecular and atomic hydrogen interaction with single crystal metal surfaces

proposed that, in the present case, oxygen hydrogenation to water occurs when exposing the layer to H atoms.
3. Molecular and atomic hydrogen interaction with single crystal metal surfaces

3.3 Structural and kinetic effects on a simple catalytic reaction: oxygen reduction on Ni(110)

Oxygen hydrogenation at 100 K by gas phase atomic hydrogen on Ni(110) has been studied under ultra-high vacuum conditions by temperature programmed desorption and X-ray photoelectron spectroscopy. Formation of adsorbed water and hydroxyl species was observed and characterized. The coverage of the reaction products was monitored as a function of both temperature and initial oxygen pre-coverage. On the contrary, when high coverage oxygen overlayers were exposed to gas phase molecular hydrogen, no hydrogenation reaction took place. The results are compared to the inverse process, exposing the hydrogen covered surface to molecular oxygen. In this case, at 100 K, simple Langmuir-Hinshelwood modeling yields an initial sticking coefficient for oxygen adsorption equal to 0.26, considerably lower than for the clean surface. Moreover, formation of hydroxyl groups is found to be twice as fast as the final hydrogenation of OH groups to water. Assuming a pre-exponential factor of $10^{13} \text{s}^{-1}$, an activation barrier of 6.7 kcal/mol is obtained for OH formation, thus confirming the high hydrogenating activity of nickel with respect to other transition metals, for which higher activation energies are reported. However, oxygen is hardly removed by hydrogen on nickel: this is explained on the basis of the strong Ni-O chemical bond. The hydrogen residual coverage is well described including a contribution from the adsorption-induced H desorption process which takes place during the oxygen uptake and which is clearly visible from the TPD data.

3.3.1 Introduction

Hydrogenation reactions on metal surfaces are expected to have a key role in a sustainable hydrogen economy based on hydrogen production, storage and burning via catalytic reactions. Hydroxyl species and water are often formed on metal surfaces as a result of dehydrogenation processes or as a consequence of reactions between co-adsorbed oxygen and hydrogen-containing molecules like alcohols, NH$_3$ etc. [123].
Therefore, a thorough study of the kinetics and chemistry of the oxygen-hydrogen interaction is a crucial step for the understanding of many catalytic processes.

Among the different transition metals used as catalysts, Ni has the advantage of being an excellent low cost methanation catalyst [124]. On Ni surfaces, oxygen chemisorbs dissociatively, forming strong chemical bonds and leading to surface reconstructions and to the growth of surface oxide layers. In particular, on Ni(110), several long-range ordered structures are formed, all involving a substrate reconstruction [125-129]. More specifically, added row substrate rearrangement characterizes the (3x1) at 0.33 ML, (2x1) at 0.5 ML and (3x1) at 0.67 ML oxygen coverage [125,126,128] with oxygen atoms always adsorbed in the long-bridge sites [126]. Below 450 K, an ordered structure with (9x5) symmetry (1.0 ML) grows for exposures between 3 and 20 L [129], while NiO layers form for larger oxygen doses.

Hydroxyl groups adsorbed on Ni(110) in the long-bridge site form an ordered p(2x1) overlayer (0.5 ML): OH groups can be obtained from the reaction of the low coverage (3x1)-O phase with water at 350 K [130].

Exposure of Ni(110) to water vapor at low temperature (100 K) initially yields the formation of an ordered H2O overlayer with c(2x2) symmetry and at 0.5 ML coverage [131]. Subsequently, a second water layer forms, which is followed by the growth of an ice multi-layer [132]. Adsorbed oxygen, hydroxyls and water have been studied by XPS and the role of radiation damage has been investigated by using a conventional Mg anode X-ray source [131]. The analysis of the intensities of the O 1s components as a function of time under exposure to the x-ray beam reveals unambiguously that photon-induced water dissociation occurs. These effects become observable already on time scales of few minutes [131].

Turning now to hydrogen interaction with Ni(110), both atomic and molecular adsorption have been studied [15,133-142]. Several ordered structures form upon exposure of the surface at low temperature (100 K): a c(2x6), a c(2x4), two c(2x6), a (2x1) and a (1x2) with corresponding coverage of 0.33, 0.5, 0.67, 0.83, 1.0 and 1.5 ML, respectively. Pairing-row surface restructuring is involved in the latter case. An even higher hydrogen coverage (up to 4 ML) can be obtained using an atomic hydrogen beam [15].

Oxygen and hydrogen co-adsorption (both molecularly dosed) has previously been studied by STM [127]: at an oxygen surface coverage below 0.5 ML, strong lateral repulsions yield to the formation of separate (2x1)-O and (1x2)-H structural domains. On the contrary, for an oxygen pre-coverage of 0.5 ML or more, hydrogen dissociative chemisorption is inhibited, because of a site-blocking effect. In this case oxygen titration begins from the surface defects [127].
In the present section I show that the peculiar reactivity of gas phase hydrogen atoms can significantly affect the reduction reaction. Moreover, I describe how structural, electronic and co-adsorption effects significantly affect the examined reaction trends.

### 3.3.2 Experimental setup

Experiments have been carried out in the new UHV setup with the rotary flange described in Section 2.1.2. The atomic hydrogen beam was generated with the aid of the home made Bischler and Bertel type thermal cracker described in Section 2.2. The sample was mounted on a four degrees of freedom manipulator by two tantalum wires which allowed resistive heating to 1300 K and liquid nitrogen cooling down to 100 K. Great efforts have been done in order to obtain a clean and ordered Ni(110) surface. Sputtering cycles with Ar+ were followed by surface annealing up to 1300 K. Oxygen treatments were not performed because total removal of the oxygen by simple titration with hydrogen was not successful. Oxygen traces were still visible in the O 1s XPS spectra and a poor (3×1) LEED pattern was present when trying to reduce oxygen with H₂. Therefore, only sputtering and annealing cycles were used to produce a contaminant free surface. Surface order and cleanliness were checked by LEED and XPS respectively. Additional confirmation for the absence of contaminants was obtained by reproducing hydrogen desorption spectra [136], which are known to be highly sensitive to surface impurities. All TPD spectra were performed with a linear temperature ramp of 2 K/s, while XPS spectra were collected at a surface temperature of 100 K and a pass energy of 20 eV. After normalisation and background subtraction, the XPS spectra were fitted with Doniach-Sunjic line shapes convoluted with a Gaussian function [92]. Binding energies were calibrated with respect to the clean Ni 2p½ peak at 852.3 eV.
3.3.3 Results and discussion

Hydrogenation of oxygen overlayers

In Figure 3.19, series of hydrogen and water TPD spectra are shown. Experiments were performed after exposure of the oxygen pre-covered Ni(110) to atomic (a) and molecular (b) hydrogen at 100 K.

Oxygen exposures and adsorption temperatures were chosen in order to obtain the ordered structures which originate upon exposure of the Ni surface to O$_2$ [125,126,128]. In addition, also the clean and the oxidised (2.0 ML) surfaces were included in this study. The hydrogen dose was fixed to 10 L in both cases, corresponding to a saturation coverage of 1.5 (molecular H$_2$) and 1.7 ML (atomic H) on the clean surface. Three peaks are present in the mass 2 TPD spectra (at 220, 285 and 330 K respectively), in agreement with previous results [143,144].

When dosing atomic hydrogen on the surface which has been pre-covered with less than 0.5 ML of oxygen, a new feature grows at 135 K, while a peak develops at 355 K in the water desorption spectra. At 0.5 ML oxygen coverage, significant changes in the desorption features are observed. New peaks develop in the mass 2 spectra at 160 and 230 K, while the single water desorption peak moves down to 240 K.

When exposing the surface to molecular hydrogen, on the contrary, almost no water desorbs from the mixed overlayer. In this case, it is known that the reaction front is limited to the island boundaries [127]: repulsive lateral interactions lead to the formation of separate O and H phases. When the oxygen pre-coverage is above 0.5 ML, molecular hydrogen dissociative adsorption is inhibited and mass 2 signal is not detected in the TPD experiments. Finally, on the NiO layers at 2.0 ML oxygen coverage, neither H atoms nor H$_2$ molecules can stick.

In Figure 3.20, the phase diagram obtained from the analysis of the LEED patterns as a function of temperature and oxygen pre-coverage is shown. Atomic hydrogen (10 L) was dosed on the oxygen pre-covered surface. At very low O coverage ($\theta_O < 0.33$ ML) and temperature ($T < 250$ K), the symmetry is that an ordered hydrogen overlayer, including the H-induced surface reconstruction. In all the other cases, oxygen dominates, yielding the known surface reconstructions.
3. Molecular and atomic hydrogen interaction with single crystal metal surfaces

Figure 3.19 - Mass 2 (left) and 18 (right) TPD spectra obtained after oxygen and hydrogen adsorption on Ni(110) at 100 K: (a) after dosing 10 L of atomic hydrogen on the oxygen pre-covered surface; (b) after dosing 10 L of molecular hydrogen on the oxygen pre-covered surface; (c) after dosing molecular oxygen on the hydrogen pre-covered surface. The oxygen pre-coverage/dose is indicated for each TPD curve. In (a) and (b), corresponding ordered oxygen overlayers are (3×1)-O at 0.33 ML, (2×1)-O at 0.5 ML, (3×1)-O at 0.67 ML and (9×5)-O at 1.0 ML.

In Figure 3.21, the hydrogen and water coverage obtained from the spectra in Figure 3.19 (a) and (b) is shown as a function of the oxygen pre-coverage. The results have been obtained after normalisation and integration of the TPD curves. The most
evident differences are visible for oxygen coverage above 0.5 ML, where H₂ does not stick, while H adsorption leads to water production.

![Phase diagram](image)

**Figure 3.20** - Phase diagram obtained by analysis of the LEED patterns as a function of the surface annealing temperature and oxygen coverage after atomic hydrogen adsorption (10 L) on the oxygen pre-covered surface. The lines are obtained from a qualitative analysis of the diffraction patterns and are drawn to separate regions where different structures dominate. It has to be reminded that there is indeed a gradual transformation of the LEED patterns from one symmetry to another.

**Figure 3.21** - Hydrogen and water surface coverage obtained from the TPD data in Figure 3.19 (a) and (b).
O 1s core-level spectra were collected as a function of the annealing temperature and oxygen coverage. For pure oxygen overlayers with coverage below 0.5 ML, a single O 1s contribution is present at 530.1 eV. When the oxygen coverage exceeds 0.5 ML, the O 1s binding energy shifts to lower values, reaching 529.5 eV at 1 ML.

![Graph showing O 1s core level binding energy as a function of oxygen surface coverage.](image)

**Figure 3.22** - O 1s core level binding energy as a function of oxygen surface coverage.

In Figure 3.23, the deconvolution of the O 1s spectra recorded during the experiment of the hydrogenation of the (2×1)-O (0.5 ML) and (9×5)-O (1 ML) structures is shown. After exposure of the surface to the H atoms beam, two new features grow at binding energies of 532.6 and 531.0 eV, which are attributed, on the basis of previous data [123,131], to adsorbed water and hydroxyl groups, respectively. Indeed, upon direct water adsorption, two O 1s peaks grow at 532.6 (533.2) and 531.2 (531.6) eV, attributed to water and OH respectively [123,131].

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Figure 3.23 - O 1s XPS spectra for two selected experiments, where (a) the (2×1)-O (0.5 ML) and (b) the (9×5)-O (1.0 ML) structures were exposed to 10 L of H atoms at 100 K and subsequently annealed to the indicated temperatures.

**Oxygen adsorption on the hydrogen-covered surface**

Dissociative oxygen adsorption at 100 K on the atomic hydrogen pre-covered surface (10 L - 1.7 ML) was studied as a function of the oxygen exposure and surface temperature. In Figure 3.19 (c), TPD spectra for masses 2 and 18 are shown. When up to 5 L of oxygen are dosed on the hydrogen covered surface, a new feature grows up in the H₂ desorption spectra at 170 K, while for longer exposures (up to 90 L) a single peak is present in the 190-220 K range, depending on the oxygen dose. TPD spectra show that water is formed: a small peak is present in the mass 18 desorption curves at 360 K for low oxygen exposures; for O₂ doses larger than 10 L, a broad asymmetric peak grows at about 275 K.

A quantitative analysis of the TPD spectra (Figure 3.24) shows a continuous growth in water production for increasing oxygen exposures. This is associated with a decrease in the residual hydrogen coverage. It is remarkable to observe that the total
hydrogen coverage (pure hydrogen and hydrogen contained in water molecules) is not conserved: this can be explained with oxygen-induced desorption of hydrogen during the $O_2$ uptake.

**Figure 3.24** - Quantitative analysis of the TPD experiments shown in Figure 3.19 (c), obtained by exposing the hydrogen pre-covered surface to molecular oxygen. The oxygen-induced hydrogen desorption is evidenced by the behaviour of the total atomic hydrogen coverage contained in molecular hydrogen and water.
Figure 3.25 - Phase diagram obtained from the analysis of the LEED patterns collected as a function of the exposure to oxygen of the hydrogen overlayer and as a function of the annealing temperature. The lines are obtained from a qualitative analysis of the diffraction patterns and are drawn to separate regions where different structures dominate. It has to be reminded that there is indeed a gradual transformation of the LEED patterns from one symmetry to another.

The surface geometry, as observed by LEED (see Figure 3.25), is governed by the hydrogen induced (1×2) row-pairing reconstruction at low temperature (below 200 K) and for oxygen exposures lower than 10 L, while in the other cases oxygen-induced surface restructuring takes place.

XPS spectra show the presence of three O 1s peaks (see Figure 3.26) for the 30 L O₂ case), in analogy to the direct experiment when atomic hydrogen was dosed on the oxygen pre-covered surface. Atomic oxygen, hydroxyl groups and water molecules O 1s binding energies are the same as for the direct experiment case.
Molecular and atomic hydrogen interaction with single crystal metal surfaces

Figure 3.26 - O 1s XPS spectra for an experiment when the surface, prepared at 100 K with exposure to 10 L of H atoms, was exposed to a 30 L molecular oxygen dose and subsequently annealed at the indicated temperatures.

Discussion

By simple inspection of the TPD data it is clear that oxygen is not easily removed by hydrogen on Ni(110). This can be imputed to the strong oxygen-metal chemical bond, which is of the order of 4.9 eV in the zero coverage limit on Ni(110) [145]. This leads to oxide layer growth for high oxygen surface densities already at low temperatures. No water is produced when reducing the oxygen pre-covered surface with molecular hydrogen, while the higher reactivity of gas phase H atoms is unambiguously proven by the formation of both water and hydroxyl groups already at 100 K. The correlation between surface reactivity and surface structure, which is mainly determined by the oxygen-induced surface reconstruction, is well evidenced. In particular, at 0.5 ML of oxygen coverage, drastic changes take place in the hydrogen-oxygen reaction. At this point, molecular hydrogen sticking and
dissociation is probably hindered by a site blocking mechanism, oxygen 1s binding energy starts shifting to lower values towards the oxide region and there is a large temperature shift of the water desorption peak in the TPD spectra (Figure 3.19b). These effects can be explained also on the basis of very local processes which lead to an effective decrease in the molecular hydrogen sticking coefficient for increasing oxygen pre-coverage. Dissociative hydrogen chemisorption is a non-activated process on clean nickel due to the presence of unoccupied d states at the Fermi energy. It has been observed that there is an attenuation of these states in the (2x1)-O phase at 0.5 ML, thus transforming H₂ dissociative adsorption into an activated process [127]. This would also explain why gas phase H atoms stick on the surface also when the oxygen pre-coverage exceeds 0.5 ML, as no dissociation barrier has to be overcome.

Figure 3.27 - Water and hydroxyl groups coverage as a function of the atomic oxygen coverage obtained from XPS data analysis. Absolute error bars of 0.05 ML on both axis are omitted for graphical clarity.
In Figure 3.27, water and OH coverage at 100 K as obtained by XPS data analysis is shown as a function of the atomic oxygen coverage for the three experiments: hydrogenation of oxygen overlayers by molecular and atomic hydrogen and oxidation of the hydrogen covered surface. The poor reactivity of molecular hydrogen is demonstrated and can be explained by a mechanism of island formation, where ordered oxygen and hydrogen domains are separated due to strong repulsive lateral interactions, in agreement with previous work [127], and on the basis of the inhibition of the molecular hydrogen dissociation. On the contrary, hydrogenation by gas phase atomic hydrogen can occur also by means of different kinetic mechanisms via a direct process (Eley-Rideal) or via a high energy precursor state (Hot Atom kinetics). It has to be remembered, as pointed out in the introduction, that during XPS measurements beam damage effects take place, inducing water dissociation [131]. A quantitative analysis of this contribution on a pure water overlayer (1 ML) shows that with a conventional Mg Kα X-ray source an initial dissociation rate of about 3×10⁻³ ML/min is obtained: this quantity clearly depends also on the photon flux, which is not reported in Ref. [131]. It is also shown that a saturation effect is present, limiting the OH/H₂O ratio to 0.6 when starting from a pure water layer. These effects are neglected in the present analysis, as their quantitative characterisation is not straightforward and depends also on co-adsorption induced effects. This assumption implies that in our experiment the XPS determined values of water and hydroxyl coverage can be ~10% lower or higher than real values, respectively. This rough estimation was obtained from data in Ref. [131] with the following assumptions: i) the dissociation rate is proportional to the surface coverage; ii) the photon flux in this experiment is of the same order than in [131]; iii) lateral and co-adsorption effects are neglected.

\[
\frac{d\theta_O}{dt} = \frac{p_{O_2}}{\sqrt{2\pi m_O k_B T}} 2s_0 \left(1 - \frac{\theta_O + \theta_{OH} + \theta_{H,O}}{\theta_{sat}}\right)^2 - k_i \theta_O \theta_H
\]  

(3.9)

\[
\frac{d\theta_{OH}}{dt} = k_1 \theta_O \theta_H - k_2 \theta_{OH} \theta_H
\]  

(3.10)

\[
\frac{d\theta_{H,O}}{dt} = k_2 \theta_{OH} \theta_H
\]  

(3.11)

\[
\frac{d\theta_H}{dt} = -2k_3 \theta_O \theta_H^2 - k_1 \theta_O \theta_H - k_2 \theta_{OH} \theta_H
\]  

(3.12)
Within this framework, reaction rates for hydrogen oxidation have been calculated on the basis of a simple kinetic model. The basic assumption is that oxygen can undergo dissociation upon adsorption on the hydrogen covered surface at 100 K (Equation 3.9). Adsorbed oxygen can thereafter react with co-adsorbed H atoms to form OH groups (Equation 3.10), which in turn further hydrogenate to water (Equation 3.11), according to a Langmuir-Hinshelwood (LH) mechanism. OH dissociation is neglected, assuming that this process is inhibited at low temperature. The hydrogen coverage (initially 1.7 ML before the oxygen uptake) is controlled by two parallel mechanisms: reaction with oxygen and adsorption-induced desorption (AID). The latter accounts for the decrease of the overall hydrogen coverage on the surface due to recombinative molecular desorption, which is caused by the sticking of oxygen. This effect is clearly visible in Figure 3.24 from the TPD data. This phenomenon was observed previously and was characterised from the kinetic point of view [146,147]. Equation 3.12, which describes the rate for hydrogen coverage variations, includes therefore also this contribution.

Figure 3.28 - Best fitting of the experimental data for the inverse experiment with the proposed kinetic model. Good agreement is found on the basis of a simple Langmuir-Hinshelwood mechanism with the addition of a contribution on the hydrogen kinetics due to the AID (see text for details). The residual hydrogen coverage is also plotted (dashed curve) as obtained from the fit.
It has also been assumed for simplicity that water, oxygen and hydroxyl groups compete for the same adsorption sites. By considering a (1×1) unit cell surface area of 2.49×3.52 Å² [130] for the gas flux normalisation in the Knudsen equation, data from the XPS experiment have been fitted according to the model by numerical integration of the rate equation ensemble (see Figure 3.28), which yields a total of five free parameters. The oxygen initial sticking coefficient obtained from the fit is $s_0=0.26$. Oxygen dissociative adsorption on the clean surface gives for $s_0$ a value which is almost unity [129]. This indicates that hydrogen pre-adsorption, which is also accompanied by an induced surface restructuring, significantly alters the oxygen interaction with the metal surface. Both species compete indeed for the same free metal $d$ states [127]. The almost constant water surface concentration for exposures above 30 L (see Figure 3.28) is explained by the lack of available residual surface hydrogen for the reaction. H is instead consumed for OH production, which is twice as fast as the final hydrogenation to water at low temperature. It is indeed found that $k_1/k_2=2$, thus indicating that, at 100 K, oxygen hydrogenation occurs at a higher rate than the second hydrogenation step to water. By assuming an Arrhenius law dependence of the kinetic parameter $k_1$ and by considering a standard pre-exponential factor of $10^{13}$ s⁻¹, a value of 6.7 kcal/mol is obtained for the activation energy of the O+H reaction. In Table 1, results from this work are compared to values reported in the literature for other transition metal surfaces. It can be observed that the hydrogenation reaction barrier Ni(110) is considerably lower than on other transition metal surfaces such as platinum and rhodium, which are though known to be good catalysts for water production via the oxygen titration reaction. These results are in agreement with the well known high hydrogenation activity of nickel, which is indeed considered as an excellent methanation catalyst. On the contrary, even if low activation barriers are found for the oxygen titration reaction on nickel, oxygen is hardly removed by hydrogen on this metal. This can be explained by the high oxygen-nickel affinity, which indeed easily drives to the formation of surface oxide layers even at low temperatures upon exposure to gas phase oxygen.
3. Molecular and atomic hydrogen interaction with single crystal metal surfaces

<table>
<thead>
<tr>
<th>Metal</th>
<th>Surface</th>
<th>ΔE_{O-H} (kcal/mol)</th>
<th>Pre-exp. (s⁻¹)</th>
<th>Ref.</th>
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<td>-</td>
<td>[149, 150, 151]</td>
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<td>[151]</td>
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<td>4×10¹¹</td>
<td>[152]</td>
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<tr>
<td>Rh</td>
<td>(110)</td>
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<td>-</td>
<td>[153]</td>
</tr>
</tbody>
</table>

**Table 1** - Activation barriers for the O+H reaction on transition metal surfaces, compared to the present work.
4 Hydrogen formation by ethanol decomposition on rhodium catalysts

4.1 Ethanol decomposition: C-C cleavage selectivity on Rh(111)

Ethanol adsorption, desorption and decomposition on Rh(111) have been studied by XPS and TPD experiments. The evolution of the C 1s and O 1s core levels spectra was monitored as a function of ethanol exposure and surface temperature. Ethanol adsorbs at low surface coverage at 90 K into two non-equivalent states, while a third species – related to multilayer formation – appears after prolonged exposures. Upon surface annealing, ethanol undergoes both desorption and dissociation, thus creating intermediate surface species which further decompose to hydrogen, carbon monoxide and atomic carbon. C-C bond cleavage is the preferential dissociation channel, while C-O bond scission is not observed. Calculations performed within the framework of the Unity Bond Index – Quadratic Exponent Potential model, have been used to test and compare different competing dissociation channels, providing an estimate of adsorption energies and dissociation barriers.
4. Hydrogen production by ethanol decomposition on rhodium catalysts

4.1.1 Introduction

Reactions of alcohols on transition metal surfaces are of relevant technological interest. Ethanol can be easily obtained in large amounts from bio-mass fermentation and its steam reforming is being considered as a viable method for hydrogen production [154]. The remarkable advantage with respect to fossil-fuel-based processes is that the overall carbon dioxide balance is neutral: the quantity of CO₂ which is produced in the process is the same as that consumed by bio-mass growth, thus creating a closed carbon cycle [154]. Efficient catalysts for ethanol steam reforming have therefore attracted great attention [155-160] and in particular new rhodium-based catalysts have recently been developed for this reaction [156,161].

Hydrogen production by low temperature reforming of oxygenated hydrocarbons - like ethanol - requires selective cleavage of the C-C bonds with respect to C-O bonds, in order to avoid undesirable alkanes formation [63]. Ethanol oxidation and dissociation on single crystal surfaces (mainly on palladium, platinum, nickel and silicon) have been widely studied in the past [63,162-167]. Ab-initio calculations and UHV experiments provided significant information on the single reaction steps as well as on the selectivity for this reaction, thus shedding light on the underlying chemical mechanisms.

On Pd(110), molecular beam experiments [162] show two competing pathways for ethanol dissociation: the molecule decomposes via a surface ethoxy species either forming a methyl group, carbon monoxide and hydrogen, or by C-O bond scission. This picture is confirmed by XPS studies [168-170]. During exposure at 130 K, a C 1s doublet shows up: the higher binding energy peak is assigned to the β carbon, adjacent to oxygen, while the other peak to the methyl group γ carbon (see Figure 4.1).

On Ni(111), TPD, Infrared Reflection Absorption Spectroscopy (IRAS) and XPS [164] show that at 90 K ethanol adsorbs molecularly, with a first layer saturation coverage of 0.2 ML. At low temperature, ethanol is bonded to the surface through both the oxygen and hydrogen atoms, with the O-H bond nearly parallel to the surface. The first step for ethanol decomposition is the O-H bond cleavage.

A study on Ni(100) [165] reveals a similar behaviour. Moreover, C-O bond scission is not observed in the reaction mechanism.

DFT calculations for ethanol on Pt(111) combined with transition state theory [63] and experiments on Pt(331) [171] and Pt(111) [64] show that the C-C bond cleaves at a higher rate than C-O.
In the literature there are only few studies of ethanol dissociation on single crystal rhodium surfaces [172-174]. On Rh(100), ethanol adsorbs molecularly at 130 K: methane production is detected upon decomposition and the formation of an intermediate oxametallacycle (CH$_2$CH$_2$O) compound is suggested on the basis of HREELS data [173]. Also on Rh(111), both desorption and decomposition occur [173,174]. TPD spectra show three ethanol desorption peaks. HREELS data indicate that ethanol binds to the surface via the OH group, which lines up parallel to the surface. In the dissociation channel, the formation of acetaldehyde is explicitly excluded, as no methane is detected in the TPD spectra. The formation of an oxametallacycle is again tentatively proposed, in analogy to the Rh(100) case. The only reaction products are carbon monoxide and hydrogen, both desorption limited. Moreover, the hydrogen desorption peak shows a persistent high temperature tail, attributed to further dehydrogenation of intermediate compounds.
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A general trend is therefore observed on transition metal surfaces: ethanol adsorbs molecularly at low temperature [171] and sequentially dissociates to ethoxide (CH₃CH₂O) and (except on rhodium) to acetaldehyde (CH₃CHO).

Here it is shown that on Rh(111) the molecule decomposes by C-C bond cleavage (no C-O cleavage is observed) and the existence of a stable intermediate reaction product is demonstrated.

4.1.2 Experimental and modeling background

Desorption experiments were performed in the general purpose UHV chamber described in Chapter 2. The background pressure was $6 \times 10^{-11}$ mbar. Ethanol was dosed through a leak valve and a 5 mm diameter stainless steel tube ending at a distance of 1 mm from the sample surface. Real-time high-resolution XPS measurements were performed at the ELETTRA SuperESCA beamline (see Chapter 2). C and O 1s core levels spectra were collected using photon energies of 400 and 650 eV, respectively, corresponding to an overall energy resolution of 250 (350) meV in the carbon (oxygen) 1s region. The base pressure in the beamline experimental chamber was about $2 \times 10^{-10}$ mbar. Ethanol was dosed by a leak valve through a microchannel array doser positioned at about 1 cm from the sample surface.

In both experimental systems, ethanol (99.8 % purity) was pre-distilled, stored in a pyrex tube and then further purified by several freeze-pump-thaw cycles. To exclude possible oxygen or water contamination, ethanol TPD spectra from a clean surface were compared to those obtained from an oxygen pre-dosed surface. Drastic changes were detected already at very low oxygen pre-coverage (0.1 ML), whereas pure ethanol TPD spectra were comparable to those reported in the literature [172-174] (see Section 4.2).

The sample was cooled by liquid nitrogen, heated resistively during the TPD experiments (2 K/s) and by hot filament irradiation for the XPS measurements (0.5 K/s). The surface was cleaned by repeated cycles of Ar⁺ sputtering, annealing to 1300 K, oxygen treatments and final hydrogen reduction. Sample cleanliness and surface order were checked by XPS and LEED respectively.

Several possible pathways for ethanol dissociation on this surface have been considered for modelling. Adsorption energies and reaction barriers were calculated within the framework of the UBI-QEP model (see Section 2.3) [52,53]. As the only inputs of the calculations, values of adsorption (atomic and molecular) [175,176], bond and dissociation energies [61,60] were taken from the literature. When not available, atomic adsorption energy values in differently coordinated sites were evaluated using
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the UBI-QEP model. Unknown molecular adsorption energies were instead calculated from the atomic binding energies.

4.1.3 Results and discussion

Low temperature ethanol adsorption

Figure 4.2 shows the TPD spectra obtained after ethanol adsorption on the clean surface at 90 K. At low exposures up to 0.125 L there are no mass 31 desorption features in the TPD spectra, indicating that all the adsorbed ethanol undergoes dissociation.

![Figure 4.2 - TPD spectra for ethanol, hydrogen and carbon monoxide after adsorption of ethanol at 90 K on the clean surface; curves are shown for increasing initial surface coverage (bottom to top), after exposures of 0.025, 0.05, 0.125, 0.25, 0.5, 1, 2 and 4 L respectively; heating rate is 2 K/s.](image)

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For increasing exposures, a peak starts growing at 230 K and shifts to lower temperatures (down to 210 K). This peak, which saturates at about 2 L, is attributed to the first layer of chemisorbed ethanol. A second peak at 166 K starts growing above 0.5 L and has not saturated yet at 4 L (the maximum used dose); this feature is attributed to the ethanol multilayer, in agreement with previous results [172,174]. The decomposition products are hydrogen and carbon monoxide: methane has not been detected in the TPD spectra. Mass 2 desorption spectra are similar to those obtained after hydrogen adsorption on the clean surface [177]. For carbon monoxide, the process is desorption limited too and the spectra show a single peak at 480 K. No increase in hydrogen and carbon monoxide formation is observed for exposures above the 210 K peak saturation dose.

Figure 4.3 - C 1s (a) and O 1s (c) XPS spectra collected during ethanol uptake at 90 K; in the central panel (b) the intensities of the different contributions to the spectra obtained after deconvolution are shown.
Figure 4.3 shows the results of the real-time XPS experiments during ethanol uptake at 90 K. XPS spectra have been fitted, after linear background subtraction, with Doniach-Sunjic function convoluted with a Gaussian function [92]. For the ethanol C 1s contributions at 90 K, best fits were obtained using a Lorentzian width $\Gamma$ of 0.2 eV and a Gaussian contribution $G$ of 0.8 eV. From the fitting procedure, a very low value for the asymmetry parameter of the ethanol carbon C 1s peaks was found, in agreement with previous results [178]. Oxygen O 1s contributions, on the contrary, showed a Gaussian width and an asymmetry which depended on the species. C on O 1s binding energies, which have been obtained after the deconvolution of the XPS data, are reported in Table 4.1.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Species</th>
<th>Temperature range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>286.9</td>
<td>Stable intermediate</td>
<td>250 - 400</td>
</tr>
<tr>
<td>286.3</td>
<td>Ethanol $\beta$ carbon (multilayer)</td>
<td>90</td>
</tr>
<tr>
<td>286.0</td>
<td>Carbon monoxide</td>
<td>250 - 450</td>
</tr>
<tr>
<td>285.7</td>
<td>Ethanol $\beta$ carbon (low coverage)</td>
<td>90 - 300</td>
</tr>
<tr>
<td>285.3</td>
<td>Ethanol $\beta$ carbon (intermediate coverage)</td>
<td>90 - 300</td>
</tr>
<tr>
<td>284.7</td>
<td>Ethanol $\gamma$ carbon (multilayer)</td>
<td>90</td>
</tr>
<tr>
<td>284.4</td>
<td>CH$_3$/CH</td>
<td>250 - 400</td>
</tr>
<tr>
<td>284.3</td>
<td>Ethanol $\gamma$ carbon (low coverage)</td>
<td>90 - 300</td>
</tr>
<tr>
<td>283.9</td>
<td>Ethanol $\gamma$ carbon (intermediate coverage)</td>
<td>90 - 300</td>
</tr>
<tr>
<td>283.7</td>
<td>C/CH</td>
<td>400 -</td>
</tr>
<tr>
<td>283.3</td>
<td>C</td>
<td>400 -</td>
</tr>
<tr>
<td>O 1s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>532.0</td>
<td>Ethanol (intermediate coverage)</td>
<td>90 - 300</td>
</tr>
<tr>
<td>530.8</td>
<td>CO?</td>
<td>250 - 400</td>
</tr>
<tr>
<td>529.6</td>
<td>Ethanol (low coverage) +?</td>
<td>90 - 450</td>
</tr>
</tbody>
</table>

Table 4.1 - Position of the C and O 1s contributions to the XPS experimental spectra, as obtained by least square fitting of the data: attribution to the different surface species is reported.

The C 1s core level spectrum (Figure 4.3a) shows initially two contributions at 284.3 and 285.7 eV, attributed to the methyl (CH$_3$-) and methydroxyl (-CH$_2$OH) carbons, respectively. This assignment is based on previous XPS results for ethanol adsorbed on Pd(110) [162] and gas phase ethanol [169,170].

These two components are the only ones present for exposures below 0.15 L and can be associated with an ethanol species which undergoes complete dissociation upon annealing, as confirmed by the absence of the mass 31 signal in the TPD spectra (Figure 4.2).
A second doublet of C 1s features, at 283.9 and 285.3 eV, appears at higher exposures (0.15-0.32 L) and is attributed to the ethanol molecules desorbing at 210-230 K. C 1s spectra of the ethanol uptake sequence could not be fitted directly with just one couple of C 1s contributions with shifting binding energies: when adopting this strategy, in fact, poor agreement was found with the least square fitting procedure and large, unphysical values of the asymmetry parameter where found for increasing coverage.

The corresponding O 1s XPS spectra, measured during the uptake, show two contributions (Figure 4.3c), at 529.6 eV and 532.0 eV, respectively. The former peak grows rapidly, saturates above 0.15 L and is therefore associated to the ethanol species of the first layer which decomposes upon annealing; the latter peak grows at higher coverage and is therefore associated to the ethanol species desorbing at 210-230 K in the TPD spectra. The binding energy difference between the two O 1s contributions is remarkably high (2.4 eV): similar O 1s differences for two non-equivalent surface species have already been observed, e.g. for molecular methanol adsorption [179]. Moreover, the observed difference in the relative peak intensity ratios at the C and O 1s regions can be attributed to photoelectron diffraction effects. In fact, it has already been shown that strong variations in the peak intensities due to diffraction effects can be observed when investigating hydrocarbon molecules, for example ethylidyne (C\(_2\)H\(_3\)) on the same surface [180]. For this reasons, peak intensities were not compared with those obtained from known adsorbate adlayers to estimate surface coverage.

In order to study the multilayer growth, a second ethanol uptake was performed at 90 K with larger ethanol exposures; in Figure 4.4, selected spectra from the complete sequence are shown. The individual components of the spectra are shown in the figure: at the largest dose (2.57 L), the multilayer related peaks, at 284.7 and 286.3 eV, predominate.

**Ethanol desorption and decomposition**

In order to promote ethanol desorption and decomposition, after exposure to 0.3 L of ethanol at 90 K, the surface was heated up to 600 K, using a linear temperature ramp (0.5 K/s).
Figure 4.4 - Selected C 1s spectra obtained during ethanol uptake at 90 K upon long exposure: the formation of the multi-layer can be observed in the top spectrum. The deconvolution of the spectra obtained from the fitting procedure is shown.

C and O 1s spectra recorded during Temperature Programmed-XPS (TP-XPS) experiments [181] are reported in Figure 4.5; the intensities of the different components of the spectra, obtained from the fitting procedure, are shown in Figure 4.6b as function of the annealing temperature. Firstly we consider the C 1s region. The intensities of all four C 1s peaks related to the ethanol first layer go to zero between 200 and 300 K, in agreement with the TPD spectra. From 156 to 300 K, three new peaks grow, at 284.4, 286.0 and 286.9 eV, and remain almost stable in the 300-400 K temperature range. The 284.4 eV peak is attributed, by analogy with results obtained for methane dissociation on platinum [178], to adsorbed CH, species originated from C-C bond cleavage of the ethanol molecule. The 286.0 eV peak is due to on-top carbon monoxide [82,182-185], formed upon dissociation of ethanol via an intermediate compound, associated to the 286.9 eV peak. The intensity of the CO related peak decreases between 430 and 480 K, in parallel with the mass 28 desorption peak in the
TPD spectra. Further C 1s contributions set in at higher temperatures (above 400 K), at binding energies of 283.7 and 283.3 eV and are assigned to CHx or surface carbon species, on the basis of previous results [178,186-188].

Figure 4.5 - Real-time C 1s (left) and O 1s (right) sequences collected during two equivalent ethanol desorption/decomposition experiments upon surface annealing.

We turn now to the O 1s spectra collected during ethanol desorption and dissociation (Figure 4.5 and 4.6b). Due to the larger intrinsic photoemission line-width of the oxygen core level, it's most likely that the spectra contain unresolved features, making therefore their interpretation not straightforward. The spectra have been fitted using three components, the two present in the uptake spectra (529.6 and 532.0 eV) plus a third peak at 530.8. The intensity of the 532.0 eV component starts decreasing at 170 K and vanishes at 300 K. In parallel, the intensity of the 529.6 eV peak decreases to about 2/3 of its original value and the third peak (530.8 eV) appears in the spectra: this corresponds to desorption and dissociation of the two ethanol species initially present on the surface. The peaks at 529.6 and 530.8 eV disappear between 400 and 450 K. The peak at 529.6 eV can be tentatively attributed to the ethanol species which
4. Hydrogen production by ethanol decomposition on rhodium catalysts

undergoes dissociation and to the reaction intermediate for temperatures above 250 K. The remaining feature at 530.8 eV could be attributed to carbon monoxide. C 1s data show that CO is adsorbed in on-top sites: this could appear to be in contrast with the related O 1s binding energy of 530.8 eV, which should be of about 531.5 eV, as reported in the literature [182]. However, while the C 1s binding energy is found to be very weakly sensitive to surface coverage and lateral interactions [183], the oxygen 1s binding energy could be more influenced by co-adsorption effects.

Figure 4.6 - TPD spectra (a) and intensities of the O and C 1s components obtained after deconvolution of the XPS spectra for ethanol desorption/decomposition (b).
Figure 4.7 - Plot of the adsorption energies and reaction barriers for the best decomposition path for ethanol dissociation: results are from UBI-QEP based calculations on Rh(111) - top panel. Modelling of the best dissociation channel - bottom panel.

Calculations

The UBI-QEP model, despite its simplicity, has been successfully used in several cases to estimate adsorption and reaction energies [53,61], even though it is known that care has to be taken in accepting the estimated parameters [61]. In Figure 4.7 the results of the calculations for the tested reaction paths are shown. Several dissociation pathways for the ethanol molecule on the clean Rh(111) surface have been
considered. More specifically, previously proposed reaction paths have been tested, involving acetaldehyde (a), ethoxy [172,174] (b) and oxametallacycle [172] (c) intermediates, and a new reaction path has been also considered, involving formaldehyde and direct C-C cleavage (d):

\[
(a) \ CH_3CH_2OH \rightarrow CH_3CH_2O + H \rightarrow CH_3CH_2O + 2H \rightarrow CH_3 + CH_2O + 2H \rightarrow CH_2 + CHO + 3H \rightarrow CH + CO + 4H \\
(b) \ CH_3CH_2OH \rightarrow CH_3CH_2O + H \rightarrow CH_3CHO + 2H \rightarrow CH_3 + CHO + 2H \rightarrow CH_3 + CO + 3H \\
(c) \ CH_3CH_2OH \rightarrow CH_3CH_2O + H \rightarrow CH_3 + CH_2O + H \rightarrow CH_3 + CHO + 2H \rightarrow CH_3 + CO + 3H \\
(d) \ CH_3CH_2OH \rightarrow CH_3 + CH_2OH \rightarrow CH_3 + CH_2O + H \rightarrow CH_3 + CHO + 2H \rightarrow CH_3 + CO + 3H 
\]

For each reaction step, both the molecular/atomic adsorption energies and the dissociation barriers were firstly calculated, testing all the possible adsorption sites and configurations. Secondly, each dissociation pathway was characterised using the “best” values, i.e. the lowest barrier for each reaction step and the adsorption geometry of the reaction products with the highest adsorption energy. It was found that ethanol preferably adsorbs on the surface via its oxygen atom, with an adsorption energy of 1.33 eV; adsorption via the hydrogen atom is energetically less convenient, in agreement with HREELS results [172,174]. The first step of reactions (a), (b) and (c) is the dehydrogenation of the hydroxyl group, which has a dissociation barrier of 1.0 eV and an overall energy gain of 4.3 eV. This step leaves the hydrogen atom adsorbed in a threefold hollow site and the rest of the molecule attached to the surface via its oxygen atom. On the contrary, the first step of reaction (d) is the direct cleavage of the C-C bond, with a much lower reaction barrier (0.6 eV) but a lower overall energy gain (3.1 eV).

Discussion

Rh(111) shows a prevalent selectivity for the C-C bond cleavage of the ethanol adsorbed molecule with respect to C-O bond scission: carbon monoxide is formed directly upon dehydrogenation of the methyloxyl group via a stable intermediate. A critical point of the data analysis is the assignment of the core level peaks to the corresponding atomic and molecular species present on the surface. For carbon monoxide and ethanol, this assignment has been done on the basis of a comparison with previous studies [82,168,182-185]. Here we will mainly focus on the dehydrogenation of the methyl group and on the stable intermediate species (present on the surface between 300 and 400 K) and characterized by a C 1s peak at 286.9 eV.
One important issue, that needs to be addressed first, is the possibility of photon induced dissociation. It is well established that high photon fluxes can promote photolysis, i.e. decomposition of adsorbed molecules. Therefore, ethanol stability under the photon beam was checked, leaving the ethanol covered surface under beam irradiation for several minutes with no visible effect in the XPS spectra. On the contrary, photon effects on the dehydrogenation of the methyl group on Pt(111) are already reported in the literature \[178\] and could have an influence on the observed CH\textsubscript{x} dehydrogenation process after the C-C bond cleavage upon ethanol dissociation. However, similar synchrotron radiation studies on ethanol decomposition have already been reported in the literature and no other photon induced effect was evidenced \[64,168\].

After ethanol dissociation at 200 K, a CH\textsubscript{x} C 1s peak at 284.4 eV is observed; this species is stable on the surface up to 400 K, then gives rise to the 283.7 and 283.2 eV peaks. The assignment of these peaks on the basis of the experimental data alone is not trivial, even after careful comparison with previous results. On Pt(111) \[178\], high resolution fast XPS experiments of thermal and photon induced methane dissociation show a peak at 282.8 eV, assigned to CH\textsubscript{3} and present up to 250 K, and a peak at 283.7 eV, assigned to a CH species, stable up to 430 K. DFT calculations for methane dissociation on Rh(111) \[189\] show that CH\textsubscript{2} is not a stable intermediate. Reflection Absorption Infrared Spectroscopy (RAIRS) experiments of the dissociation of the methyl group on Rh(111) \[186,187\] report on the stabilizing effect of carbon monoxide for C\textsuperscript{=}, up to 475 K. Finally, HREELS data \[188\] reveal the formation of CH above 420 K. The peak at 284.4 eV could be therefore due to CH\textsubscript{3} which is stabilized by the presence of co-adsorbates like carbon monoxide, while peaks at 283.7 and 283.2 eV could be attributed to CH and atomic carbon. An alternative interpretation is that the peak at 284.4 eV is due to CH\textsubscript{2}; this would imply that when C-C bond cleavage occurs, CH\textsubscript{3} is not stable, either because of the temperature or of the beam irradiation; in this case, the lower binding energy peaks observed at higher temperatures would be due to non-equivalent surface carbon species; this picture is in agreement with DFT calculations on methane dissociation \[189\]. The latter interpretation is further supported by the model calculations (Figure 4.7). Within this framework, a direct comparison of the first reaction step energy barriers clearly favours pathway (d), which involves formaldehyde formation. More in detail, by assuming a standard pre-exponential factor of 10\textsuperscript{13} s\textsuperscript{-1}, energy barriers from the UBI-QEP model and a temperature ramping rate of 2 K/s as in the experimental conditions, it is easy to compare the first steps of the reaction pathways which involve C-C (d) and O-H ((a) to (c)) bond scission respectively. An initial ethanol coverage of 0.25 ML is arbitrarily assumed, without consequences on the simulation output as lateral interactions are
not considered by the model. Integration of the related rate equations shows that no ethanol actually decomposes to CH\(_3\)CH\(_2\)O\(+\)H, while it dissociates to CH\(_3\)+CH\(_2\)OH. UBI-QEP calculations favour therefore the assignment of the C 1s peak at 286.9 eV to formaldehyde as a stable intermediate. For path (d) the whole reaction was numerically simulated, again by integration of the related rate equations. Results for ethanol and CH\(_3\) species are reported in Figure 4.8: surface coverage of the selected species is shown as a function of temperature during the virtual experiment and can be therefore compared to results in Figure 4.6 from TPD and XPS. CH\(_3\) and CH\(_2\) are not stable species when formed upon ethanol dissociation at room temperature and decompose to CH. The modelling of the reaction supports hence the assignment of the 283.7 and 283.2 eV C 1s peaks to surface carbon and the 284.4 eV peak to CH.

![Graph](image)

**Figure 4.8** - Results from the integration of the rate equations for reaction path (d): CH\(_3\), which is formed upon ethanol dissociation at room temperature, is not stable and dissociates to CH.

There is already some experimental work reported in the literature about formaldehyde adsorption and decomposition on Rh(111) [190]: however, HREELS and TPD experiments show that, after adsorption on the clean surface at 90 K, CH\(_2\)O undergoes rapid decomposition to carbon monoxide and hydrogen already below 130 K. On the contrary, addition of oxygen promotes polymerization of formaldehyde to paraformaldehyde with subsequent stabilisation up to 300 K. It is reasonable to propose that similar stabilization effects may take place also in this case, even though further studies are required to reach a firm conclusion. In the literature, high binding energy C 1s features have been attributed to surface acetates as in the case of ethanol.
oxidation on Pd (110) [168]. This requires the presence of co-adsorbed oxygen on the surface; since the presence of contaminants in the ethanol vapour was previously excluded (see experimental section), this explanation can be ruled out. On the other hand, C 1s features at binding energies as high as 288 eV have been reported for CH$_2$O adsorption on single crystal metal surfaces [191]. In Figure 4.7 (bottom panel) a final model for the proposed reaction path for ethanol decomposition on this surface is shown, on the basis of the reported experimental and computational results.
4.2 Ethanol auto-thermal reforming on rhodium catalysts: a comparison between model and "real" catalysis

The influence of oxygen on the decomposition of ethanol over rhodium (111) and (100) single crystal surfaces was studied by means of Ultra High Vacuum TPD experiments. Oxygen at low surface coverage (between 0.1 and 0.25 ML) promotes ethanol decomposition and the formation of carbon dioxide, while carbon monoxide production is not significantly altered, with respect to the reaction on clean samples. An oxygen coverage above 0.25 ML hinders hydrogen formation due to the prevalent oxidising action which leads to water formation. These results are in line with data obtained for ethanol decomposition over a 5% Rh/Al2O3 catalyst under typical reforming working conditions (i.e. T = 923 K and P = 1 bar), thus indicating that an oxidising environment is required in order to avoid carbon poisoning and to promote C2-containing molecules decomposition. On the contrary, excess of oxygen leads to a strong reduction of hydrogen concentration in the reaction products.

4.2.1 Introduction

As already discussed in Section 4.1.1, among other possible solutions for hydrogen production, it has been proposed to extract hydrogen from bio-ethanol, which can be easily obtained by the fermentation of vegetable bio-mass. Up to now, the energy content of the rest bio-mass which is yearly produced by human being activities is about eight times the present world energy demand [192]. Moreover, the quantity of carbon dioxide which is released in the ethanol reforming process is the same which is consumed by bio-mass growth, thus creating a closed cycle for greenhouse gas emissions [154]. Among the several fuel cell technologies which have already been developed, Molten Carbonate Fuel Cells (MCFC) operate at high temperatures (920 K) and allow the feeding by hydrogen streams which still contain a high (about 10 vol %) concentration of carbon monoxide [193]. Heat is co-generated: the thermodynamic efficiency of the electrochemical reaction at the anode (H2 + \frac{1}{2}O2 → H2O) never reaches 100 %. It has already been shown that this waste heat can be directly supplied to the reactor to sustain the endothermic ethanol reforming reaction [194]. Bio-ethanol is characterised by large water contents (from 50 to 90 wt % [195]),
4. Hydrogen production by ethanol decomposition on rhodium catalysts

which can be directly used in the steam- and auto-thermal- reforming processes (SR and ATR respectively) [193]. Studies in order to optimise the reforming reaction, maximise catalyst's life and the quantity of produced hydrogen by calibration of the water/oxygen/ethanol molar ratios are already available in the literature [156,157,160,193,196-199].

Rhodium-based catalysts have already shown good selectivity towards the C-C cleavage reaction for ethanol decomposition. However, deep comprehension of the chemical and kinetic mechanisms governing a reaction is not straightforward. Most surface science techniques work indeed at low pressure regimes, where reaction conditions and parameters can be substantially different with respect to the “real” catalytic reaction. Therefore, a comparison between results from a model reaction under ultra high vacuum (UHV) conditions and the ethanol oxidation on a supported catalyst under high pressure regimes (1 bar) can yield further insight into the reaction mechanisms. Here, I will focus on the influence of oxygen on ethanol decomposition for hydrogen production: a comparison between reactions under UHV and “typical” conditions is made. In the former case, after ethanol adsorption on the clean and oxygen pre-covered surfaces at 90 K, TPD experiments were carried out and the influence of oxygen on the reaction products was investigated. These results are compared to data obtained from ethanol reforming on a 5% Rh/Al2O3 catalyst under pure ethanol and water/ethanol streams: these measurements were performed in the framework of a collaboration established ad hoc with a research group of the CNR-TAE institute in Messina (Italy). In the latter reforming case, water is expected to dissociate on the catalyst at temperatures as high as 900 K and only adsorbed oxygen and very short lived hydrogen are actually present. This is not true any more for the UHV experiment at low temperature, where water can exist also in the molecular form on the surface. Therefore, from the surface chemistry point of view, the direct use of oxygen has been chosen in the model experiment for better reproducing the real case. The aim of this last part of my work is to qualitatively compare the behaviour of an interesting catalytic reaction under different regimes. In particular, a qualitative comparison between model and “real” catalysis is done for ethanol auto-thermal reforming on rhodium catalysts.

4.2.2 Experimental setups

UHV experiments

Desorption experiments were performed in the general purpose UHV chamber described in Chapter 2. Ethanol was dosed and treated as described in Section 4.1. The samples were cleaned as described in Section 4.1.2. All TPD
experiments were carried out with a linear temperature ramp of 2 K/s. The coverage of the adspecies was determined by integration of the TPD mass signal, normalisation for the relative RGA sensitivity factors and subsequent rescaling with respect to the coverage of the known hydrogen and carbon monoxide adlayers. Oxygen coverage was calibrated by means of XPS, relatively to the known coverage of the ordered structures which are formed by oxygen atoms on rhodium (111) [91] and (100) [200] surfaces. Ethanol uptakes on the surfaces pre-covered with 0.25 and 0.5 ML of oxygen were indeed performed on the corresponding ordered adlayers.

Rh supported catalyst preparation and characterisation, ethanol steam- and auto-thermal-reforming

Before any treatment, the support (γ-Al₂O₃) was stabilised by calcination in air for 3 h at T = 973 K. The rhodium supported catalysts were prepared by incipient wetness impregnation of the support with a solution of rhodium acetylacetonate in benzene medium. After impregnation, the powder was dried at 350 K and calcined at 600 K for 12 h. Finally, the solid was pressed under P = 400 kg/cm², crushed and sieved, and the 40-70 mesh fraction was used for the catalytic tests. X-Ray Fluorescence (XRF) analysis, carried out with a Philips PW 1400 instrument, showed an effective rhodium sample concentration of about 5-6 wt %.

Temperature Programmed Reduction (TPR) has been carried out by using a mixture of H₂ (5 vol%) in Ar (95 vol%).

Experimental, “real” working conditions tests were performed at atmospheric pressure in a fixed-bed linear quartz microreactor (i.d. = 4 mm; H_bed = 1.0-2.0 cm). 0.010 - 0.060 g of catalyst (grain size: 40-70 mesh) diluted with 156 - 300 mg of similar sized carborundum (SiC) were used for the catalytic reaction tests. Before each run, the catalyst was reduced “in-situ” at T = 725°C for 1 h under flowing hydrogen and then cooled down to the reaction temperature. Water/ethanol mixture was vaporized at 120°C in a stream of N₂. Experiments were performed at temperatures ranging from 823 to 923 K; Gas Hourly Space Velocities (GHSV) ranging from 5×10³ to 3×10⁵ ml EtOH h⁻¹ mlcat⁻¹ and steam to carbon ratios ranging from 2.1 to 6.2 mol/mol were used. For clarity, only selected experiments are reported here. Base-line prefixed conditions were: T = 923K; S/C = 4.2 mol/mol; O/C = 0.19 mol/mol and GHSV = 10⁵ h⁻¹. The O/C molar ratio is defined as the inlet ratio between the molecular oxygen and the ethanol feed (O₂/C₁₂H₂₅OH).

The Rh/Al₂O₃ catalyst produces only a little amount of coke under experimental conditions. In particular, no more than 0.27 mg coke h⁻¹ gcat⁻¹ can be deposited under steam reforming conditions, while in presence of some oxygen, no coke at all can be observed (neither by TEM analysis) for “short-time” tests. To
further minimize the coke influence, data reported in this section have been recorded after 30 min on stream and represent the first recordable data from the fresh activated catalyst. The gas-chromatographic analysis, made before and after the reaction bed, confirms that no coke is formed, because of the goodness of the carbon mass balance (close to 100%).

4.2.3 Results and discussion

UHV desorption experiments

In Figure 4.9, TPD spectra obtained after ethanol adsorption at 90 K on the two single crystal surfaces are reported. For exposures below 0.125 L, no ethanol desorption peak is detected, indicating that all the adsorbed ethanol undergoes dissociation; on the contrary, in agreement with previous experiments [172], at higher surface coverage there are two competing pathways including both desorption and dissociation. On Rh(111), a peak at 225 K appears in the TPD spectra after 0.25 L ethanol exposure, shifting down to 210 K for longer exposures (up to 4 L). This peak is attributed to ethanol molecules which are directly bonded to the metal surface after low temperature (90 K) adsorption. At higher doses a new, sharp peak appears at 155 K due to molecules desorbing from the ethanol multilayer (see Section 4.1).

Figure 4.9 - Mass 31 TPD spectra for increasing exposures to ethanol of clean Rh(111) (left) and Rh(100) (right) at 90 K.
On Rh(100), three desorption peaks show up in the TPD spectra. The low temperature one (156 K) is attributed to the multilayer, while the other features at 190 and 225 K could be tentatively related to two non-equivalent ethanol species adsorbed on the surface, as well as to the ethanol second and first layer, respectively. A small shoulder is indeed present at 170 K also in the desorption spectra from Rh(111), but is not well resolved due to the lower temperature position of the main first layer desorption peak.

Figure 4.10 - Hydrogen (mass 2) TPD spectra after ethanol adsorption on clean and oxygen pre-covered (111) and (100)Rh surfaces at 90 K. Spectra corresponding to both surfaces are shown as a function of ethanol exposure and oxygen coverage.
4. Hydrogen production by ethanol decomposition on rhodium catalysts

Ethanol binds more strongly to Rh(100) than to Rh(111), desorbing at a temperature which is about 15 K higher in the former than in the latter case. As already reported in the literature [172-174], ethanol main decomposition products on the two clean surfaces are hydrogen and carbon monoxide. On Rh(111) methane production is not observed, while some CH₄ is produced on Rh(100).

When oxygen is present on the surface prior to ethanol adsorption at low temperature, the reactions change quite significantly. The oxidation experiments were performed only upon ethanol doses below 0.5 L in order to populate only the ethanol first layer. In Figure 4.10 it is shown how hydrogen (mass 2) production changes as a function of ethanol exposure and oxygen coverage. On the clean surfaces, a single main desorption peak is present at 275 and 300 K on Rh(111) and Rh(100) respectively, indicating that the main hydrogen peak is desorption limited in agreement with data from the literature [172-174]. When a small oxygen amount is present on the surface, a new peak grows in the spectra from the two surfaces, at 400 and 375 K respectively. The overall hydrogen amount produced from ethanol decomposition increases, with respect to the clean surfaces, for an initial oxygen coverage of 0.1 or 0.25 ML; on the contrary, when the oxygen surface coverage is further increased (up to 0.5 ML), hydrogen production drops due to the prevailing oxidising reactions and water is produced instead.

On Rh(111), three water desorption peaks grow in the mass 18 TPD spectra for increasing oxygen coverage at 170, 240 and 420 K respectively. Four peaks are present in the same conditions on Rh(100) at 165, 225, 275 and 340 K (see Figure 4.11). Small water features are present in the desorption spectra obtained after ethanol adsorption on the clean surface: this is attributed to the EtOH cracking into the detector. Oxygen reacts with residual carbon and carbon monoxide, leading to a growing production of carbon dioxide as the initial oxygen surface coverage is increased.

This trend can be observed in Figure 4.12, where CO₂ (mass 44) TPD spectra are reported for both surfaces. As for hydrogen, the low temperature features are due to desorbing ethanol which undergoes dissociation into the RGA. The two main CO₂ desorption peaks on Rh(100) are at 340 and 460 K, while a broad shoulder is present at 600 K for high oxygen coverage and low ethanol exposures. On Rh(111), three peaks can be distinguished at 395, 415 and 460 K respectively. Carbon monoxide desorption (not shown) is not altered by oxygen addition on Rh(111) and only one peak is visible in the TPD spectra at 475 K. On Rh(100), a single peak at 500 K is visible on the clean surface, while upon oxygen addition a new peak grows at 340 K. Methane has been excluded in the past as a by-product of ethanol decomposition on clean Rh(111) [172,174], while, accordingly to Ref. [173] some traces are present on Rh(100).
Figure 4.11 - Water (mass 18) TPD spectra after ethanol adsorption on clean and oxygen pre-covered (111) and (100) Rh surfaces at 90 K. Spectra corresponding to both surfaces are shown as a function of ethanol exposure and oxygen coverage.
4. Hydrogen production by ethanol decomposition on rhodium catalysts

Figure 4.12 - Carbon dioxide (mass 44) TPD spectra after ethanol adsorption on clean and oxygen pre-covered (111) and (100) Rh surfaces at 90 K. Spectra corresponding to both surfaces are shown as a function of ethanol exposure and oxygen coverage.
4. Hydrogen production by ethanol decomposition on rhodium catalysts

Figure 4.13 - Methane (mass 15) TPD spectra after ethanol adsorption on clean and oxygen pre-covered Rh(111) at 90 K. The contributions due to ethanol desorption have been subtracted: see text for details.

It is found that the presence of oxygen on the surface promotes methane formation on both Rh(111) and (100), with a maximum production for an oxygen coverage between 0.1 and 0.25 ML (see Figure 4.13). A single peak is present in the TPD spectra at 250 (220) K on Rh(111) (Rh(100)). Selected spectra for the (111) surface are plotted in Figure 4.13: since ethanol gives a contribution also to mass 15 due to its dissociation in the RGA, methane spectra have been obtained after normalisation and subtraction of the ethanol (mass 31) features. No other desorbing species were detected in the UHV experiments.

Quantitative information can be obtained from the TPD spectra by means of integration and normalisation of the data (see Section 4.2.2) in order to quantify the reaction products as a function of the reaction conditions (see Figure 4.14). It can be observed that less ethanol desorbs when the oxygen coverage is increased. This could be due to a twofold effect: ethanol decomposition is promoted by oxygen, while at the same time adsorption is hindered by a site blocking effect. Carbon dioxide production is also promoted by oxygen. Hydrogen production reaches a maximum for an initial oxygen coverage between 0.1 and 0.25 ML; the same trend is visible in the carbon
monoxide desorption data. From a direct comparison of the ethanol and hydrogen desorbing signals, it can be observed that the (100) surface is more reactive towards the dehydrogenation reaction: on the clean surface the ethanol reacting/desorbing ratio is about 0.27, while it is 0.18 on Rh(111). This difference is observed also in the influence of oxygen on the reaction.

Figure 4.14 - Ethanol, carbon monoxide, carbon dioxide and hydrogen production upon ethanol desorption and decomposition on (111) (left) and (100) (right) Rh surfaces as a function of the initial oxygen coverage (bottom) and ethanol exposure (colours).
When normalising the results for the different atomic surface densities, it is found that on average about 70% more hydrogen is produced on the (100) surface for the same surface area. The influence of oxygen on the production of methane can be clearly observed in the case of the (111) surface (Figure 4.14 – left panel). From the TPD data we can also estimate the amounts of residual carbon and oxygen on the surface after the reaction. This can be done by simple evaluation of the initial ethanol coverage and by subsequent subtraction of the desorbing species, providing a proper normalisation for the stoichiometry of the C and O contents. In particular, the initial EtOH coverage is given by Equation 4.1. Analogously, the residual C and O coverage is given by Equations 4.2 and 4.3 respectively.

\[ \theta_{\text{EtOH}}^{\text{res}} = \theta_{\text{EtOH}}^{\text{init}} - \left( \theta_{\text{CO}} + \theta_{\text{CO}_2} + 2\theta_{\text{H}_2\text{O}} \right) \]  

\[ \theta_{\text{C}}^{\text{res}} = \theta_{\text{EtOH}}^{\text{init}} - \left( \theta_{\text{EtOH}} + \theta_{\text{CO}} + 2\theta_{\text{CO}_2} + 2\theta_{\text{H}_2\text{O}} \right) \]  

It is found that, within the large error bar due to the error propagation, almost no residual oxygen remains on the surface after the TPD experiment. On the contrary, about 0.1-0.2 and 0.2-0.3 ML of residual carbon remain on the (100) and (111) surfaces respectively. In addition, the amount of C depends both on the initial ethanol coverage and on the oxygen pre-coverage. As expected, less contaminant is present on the surface which was initially pre-covered with a higher oxygen amount.

Ethanol auto-thermal reforming, steam reforming and dry-decomposition on supported Rh catalyst.

For a typical experiment carried out in ATR conditions (S/C = 4.2 mol/mol; O/C = 0.19 mol/mol; P = 1 bar; T = 923 K; GHSV = 10^5 h^{-1}), a decay in the activity of the supported Rh catalyst can be observed as a function of time. In a previous paper [156] this effect was attributed to particles sintering because of the hot-spots on rhodium crystallites. Indeed, the metal surface area of Rh crystallites supported on Al₂O₃ is close to 8.1 m² g_{cat}^{-1} for the fresh catalyst while it becomes 2.5 m² g_{cat}^{-1} after 100 h on oxidant stream (O/C = 0.4 mol/mol). On the other hand, without added oxygen (SR conditions), the faster catalyst decay can be attributed to the great amount of coke formed on the catalytic surface because the Rh dispersion doesn’t changes in the absence of O₂. In any case, whatever the operative conditions, the catalytic activity
changes (decreases) with time. For this reason, only the initial activity of freshly prepared samples can be directly compared.

Figure 4.15 - Ethanol decomposition and hydrogen production over a 5% Rh/Al2O3 catalyst under different feeding flows at 923 K and 1 bar.

A strong positive influence of both water and oxygen on the overall ethanol conversion is observed. Traces of water, in fact, can double the ethanol decomposition, strongly changing also the distribution of the final products. The formation of CO2 starts only in presence of water and the little amount of carbon dioxide (< 1 vol %) present when dry ethanol is used, is produced by the contribute of the water derived from dehydration (C2H5OH → C2H4 + H2O). In presence of both water and oxygen, more CO2 is formed and C2H4 disappears, probably because of simultaneous oxidation reactions.

Figure 4.15 reports the influence of the GHSV on the outlet composition. As expected, the ethanol conversion inversely depends on the GHSV, while the outlet
analysis varies as a function of the contact time ($\tau = 1/\text{GHSV}$). It is interesting to note that a great amount of hydrogen (> 50 vol %) is always formed (independently of the GHSV) and that, except than for the lowest GHSV value ($5 \times 10^3$ h$^{-1}$), only a little change on the selectivity to other (carbonaceous) products can be observed.

Discussion
The so called “pressure gap” is a major problem for comparing results from surface science to the “real catalysis” world: kinetic effects and surface structure cannot always be easily and directly correlated in the two cases. The aim of this experimental work is to qualitatively describe the behaviour under “real” and UHV conditions of the ethanol reforming reaction, which is widely known to be a good candidate for renewable hydrogen production. Additional information supplied by typical surface science experiments can significantly provide further insight into the underlying chemical and kinetic mechanisms which are involved in the process.

From UHV experimental results it is found that the presence of low oxygen coverage (less than 0.25 ML) favours ethanol decomposition with respect to desorption on a rhodium single crystal surface, thus changing in the desired direction the equilibrium between the two competing pathways (desorption and dissociation) for the molecule. At the same time, upon oxygen addition, a slight increase in hydrogen production is observed together with a decrease in ethanol desorption. In the real reforming reaction on 5% Rh/Al$_2$O$_3$, a similar behaviour is observed. Therefore, the overall qualitative influence of oxygen on the reaction trends is indeed the same both for the model and for the “real” reactions. However, it is has to be mentioned that oxygen presence significantly alters the reaction mechanism, rather than only acting as a promoter or as a simple residual carbon remover. It has already been shown that different reaction intermediates are present upon oxygen addition with respect to the dry ethanol decomposition reaction. Acetate has been identified for example as a stable intermediate below 410 K on Pd(110) when ethanol decomposition occurs on the oxygen pre-covered surface [168].

Under UHV conditions, CO production is observed in the dry ethanol decomposition reaction. When oxygen is added, carbon dioxide is formed. In order to better observe these trends, reaction products concentrations for the three experiments on Rh(100), Rh(111) and 5% Rh/Al$_2$O$_3$ respectively are plotted in Figure 4.16. Hydrogen, carbon monoxide and carbon dioxide concentrations are shown in the bottom panel for the ambient pressure experiment. For the UHV experiments, instead, in the top panel the integrated mass-spec signal after normalisation is plotted. Data are reported for reactions on both surfaces (Rh(100)-upper part, Rh(111)-lower part).
4. Hydrogen production by ethanol decomposition on rhodium catalysts

Figure 4.16 - Direct comparison of the reaction products concentrations. Reactor outlet data have been normalised with respect to the ethanol conversion efficiencies. Ethanol exposure in the UHV experiment was 0.5 L.

TPD data shown in Figure 4.13 indicate also that presence of oxygen favours CH₃ recombination with adsorbed hydrogen to CH₄, probably due to a site blocking mechanism: the methanation reaction is promoted by low (0.1-0.25 ML) oxygen surface pre-coverage. On the contrary, if oxygen is not present on the surface, methane is not detected on rhodium (111) in the TPD spectra. Some traces are instead
present upon dry ethanol decomposition on Rh(100), where oxygen addition shows the same influence as on the other surface. When methane desorption is not observed, methyl groups undergo therefore dehydrogenation. Also under “real” reforming conditions the same trend is observed, i.e. methane concentration in the outlet stream raises upon oxygen presence.
4. Hydrogen production by ethanol decomposition on rhodium catalysts
5. Conclusions

This PhD thesis is a summary of the scientific work which I performed within the surface science framework during these three years. The driving reasons for the present project were to investigate some of the critical points of chemical reactions involved in the hydrogen cycle. There is growing interest in hydrogen as a clean energy vector: this is due to several reasons which are making our fossil oil based economy critically unstable. The world growing energy demand, the development of emerging countries, the non-sustainability of the environmental impact of the combustion of the fossil fuels, the instability of the oil supplying countries and the depletion of the world’s oil reservoirs (see Figure 5.1): these are all real and valid reasons for steering towards a renewable hydrogen based economy. However, several challenging technical barriers have still to be overcome before making an efficient and convenient hydrogen economy a reality. In particular, catalytic reactions are the core of the technology needed for proper hydrogen treatment (production, storage and burning). The present study reports on some key points which have been chosen within a sea of open questions. Within the framework of this thesis work, scientific investigation has been performed with the aid of model surface science experiments. Deeper insight into the kinetics of model chemical reactions which can be of clear interest within the hydrogen chemistry has been obtained, at least from the model UHV systems point of view. This work can be divided into three main sections: the evaluation of a new method for the determination of hydrogen adsorption sites, the study of the hydrogenation kinetics on metal surfaces by gas phase hydrogen
atoms and the investigation of the decomposition pathways for ethanol on a rhodium catalyst.

Figure 5.1 – (a) Puzzle of satellite images in the visible wavelength of the earth surface during night: an idea of the geographical distribution of the energy demand; (b) carbon dioxide concentration in the atmosphere; (c) the growth of the price of crude oil barrels during the last two years; (d) the exponential growth of the world’s energy demand and the role of the different energy sources.

Hydrogen interaction with metals: an H atom is not as “easy” as it seems to be

As already discussed, hydrogen atoms adsorbed on a surface have weak scattering properties, high diffusion rates and generally show small cross sections to conventional surface science probes. This makes hydrogen-metal systems hard to study from an experimental point of view. In particular, even the simple determination of the adsorption site for an H atom on a single crystal metal surface is not straightforward. By comparing the results of SCLS analysis of the Rh 3d5/2 core level with Monte Carlo simulations, the adsorption sites of hydrogen on Rh(100) at low temperature have been determined as a function of surface coverage. At low
coverage hydrogen prefers the most coordinated hollow site, whereas with increasing densities, the bridge site becomes energetically preferred due to substrate mediated lateral interactions. It has been shown that proper coupling of the SCLS analysis with modelling of the substrate mediated lateral interactions can yield the adsorption sites for H atoms on a single crystal.

Kinetics of hydrogenation reactions

It has been explained in Chapter 1 that both adsorption (atomic or molecular hydrogen, absorption into subsurface sites) and reaction mechanisms (Eley-Rideal, Langmuir-Hinshelwood and Hot Atom) can affect a hydrogenation reaction. Atomic hydrogen interaction with metal surfaces was investigated in this work. Upon exposure of the Ru(10\,\overline{1}\,0) surface to the atomic beam at 90 K, a saturation coverage of 2.5 ML is obtained, which is higher than with conventional molecular adsorption (2.0 ML). Moreover, the saturation coverage is determined by an equilibrium between the adsorption and abstraction processes: a simple kinetic description, based on the hot atom precursor model, well reproduces the experimental data both for atomic hydrogen adsorption and deuterium abstraction, yielding values for the abstraction \((0.5\pm0.2 \text{ Å}^2)\) and adsorption \((3.3\pm0.4 \text{ Å}^2)\) cross sections which are comparable with results obtained for other surfaces. The high reactivity of atomic hydrogen is shown by hydrogenation of pre-adsorbed oxygen to water, which is not obtained with molecular hydrogen. Oxygen reduction and hydrogen oxidation reactions at low temperature (100 K) have been studied also on Ni(110). Evidence for a high reactivity of gas phase H atoms has been shown in the case of the reduction of adsorbed oxygen. The poor reactivity of molecular hydrogen is discussed on the basis of structural, electronic and co-adsorption effects. The inverse reaction, where oxygen was dosed on the hydrogen pre-covered metal surface, was also studied. In this case, a simple Langmuir-Hinshelwood mechanism is proposed to describe OH and water formation, with the addition of the adsorption-induced desorption process which accounts for hydrogen recombinative desorption during the oxygen uptake. It is found that at 100 K oxygen hydrogenation proceeds twice as fast as OH hydrogenation. The activation barrier for the first hydrogenation step is compared to data from the literature for other systems. A lower value is found, with respect to other transition metal surfaces, which are however good catalysts for the oxygen titration reaction, while oxygen is hardly removed by hydrogen on nickel. This is explained on the basis of the strong Ni-O chemical bond and of a combined structural and electronic effect, where the free metal d bands which are necessary for \(\text{H}_2\) decomposition are filled by the adsorbed oxygen electrons.
5. Conclusions

Catalytic reactions for hydrogen production

By means of high resolution real-time XPS and TPD, ethanol decomposition on Rh(111) was studied. As a main result, evidence for selectivity of this rhodium surface to C-C bond cleavage with respect to C-O bond scission was found. Final dissociation products are carbon monoxide, hydrogen and atomic carbon, in agreement with previous results. The interpretation of the spectroscopic data is supported by calculations based on the simple UBI-QEP phenomenological model, which tentatively identifies formaldehyde as the stable intermediate species between 250 and 400 K. In this temperature range, dehydrogenation of the methyl group is observed in parallel, thus explaining the absence of methane in the desorption spectra. The work is corroborated by results from experiments on a “real” rhodium-based catalyst, which have been performed in parallel with model reaction simulations on rhodium single crystals under UHV conditions. The so called “pressure gap” is a major problem for transferring results from surface science to the real catalysis world: so, the aim of this last part of the present work was to qualitatively compare the reaction trends under different pressure regimes. In particular, the role of oxygen in the ethanol decomposition process has been studied and different reaction conditions have been reproduced, including dry decomposition, steam reforming and autothermal reforming. It has been found that the presence of small oxygen amounts promote ethanol decomposition and therefore favour hydrogen formation: this is the case in both reaction conditions (ambient pressure and UHV). Qualitative agreement between the two experimental conditions has been found also for the production of carbon monoxide, carbon dioxide and methane.
References

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Acronyms

ATR - Auto Thermal Reforming
BO - Bond Order
BOC - Bond Order Conservation
DFT - Density Functional Theory
EAM - Embedded Atom Model
ER - Eley-Rideal
ESCA - Electron Spectroscopy for Chemical Analysis
HA - Hot Atom
HREELS - High Resolution Electron Energy Loss Spectroscopy
IRAS - Infrared Reflection Absorption Spectroscopy
LEED - Low Energy Electron Diffraction
LH - Langmuir-Hishelwood
MC - Monte Carlo
MCFC - Molten Carbonate Fuel Cells
MCS - Monte Carlo steps
ML - Monolayer
NMCS - number of Monte Carlo steps
RAIRS - Reflection Absorption Infrared Spectroscopy
RF - Radio Frequency
RGA - Residual Gas Analyser
SCL - Surface Core Level
SCLS - Surface Core Level Shift
SPA-LEED - Spot Profile Analysis Low Energy Electron Diffraction
SR - Steam Reforming
Acronyms

SR – Synchrotron Radiation
STM – Scanning Tunneling Microscopy
TDS – Temperature Desorption Spectroscopy
TPD – Temperature Programmed Desorption
TPR – Temperature Programmed Reduction
TP-XPS – Temperature Programmed X-Ray Photoelectron Spectroscopy
UBI-QEP – Unity Bond Index – Quadratic Exponent Potential
UHV – Ultra High Vacuum
XPS – X-Ray Photoelectron Spectroscopy
XRF – X-Ray Fluorescence
When working on a three years long project in science, there is plenty of people you meet and spend your time with. In the everyday life through the labs and university departments, the interaction with colleagues and friends is a fundamental ingredient which enriches your person. This is why I firstly want to thank in advance all the people who have worked with me during these years.

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