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Electronic structure and chemical reactivity of transition metals' pseudomorphic layers and supported nanoclusters

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Abstract

The importance of heterogeneous catalysis in chemical industry and its economic impact in today’s society motivate the continuous research effort in this field. Transition metals are among the main ingredients of commercial catalysts due to their chemical properties which depend on their surface morphological and electronic structure. It is well known that their catalytic properties can be further improved by tuning particle size in the nanometre range or by alloying different transition metals.

Nowadays it is possible to predict the variation of surface chemical properties on the basis of the $d$-band centre energy position, which is actually considered as one of the most reliable depicter of chemical reactivity. This physical quantity cannot be easily accessed by experimental measurement and is typically calculated using a theoretical approach. A promising approach to establish an experimental relationship between electronic structure and chemical reactivity relies on the use of X-ray Photoelectron Spectroscopy with third generation synchrotron radiation sources. Indeed, the high resolution achieved in the recent years has allowed the identification of the contributions originated from bulk and surface atoms in the core level photoemission spectra, thus determining what is usually named Surface Core Level Shift (SCLS). It has been shown that SCLS is a valuable probe of surface electronic structure, since the core level binding energy of an atom depends strongly on the local structural and chemical environment.

In this thesis, the electronic structure modification induced by reduced coordination, surface strain, atomic rearrangement and ligand effects are investigated in different systems by means of High Energy Resolution Core Level Spectroscopy experiments, on several systems with different complexity. Pseudomorphic states of Pd, grown on a Ru(0001) surface, have been studied by comparing the calculated $d$-band center shifts of the differently coordinated atoms to the measured core level shifts of the same species, finding a strong relationship between these two physical quantities. For two of structures (1- and 2-Pd MLs/Ru(0001)) we tested the chemical reactivity by exposing the surfaces to oxygen. The results confirmed the relationship between $d$-band center shift, CLS and chemical reactivity.

A more complex system is the one composed by Pd nanoclusters on Single Walled Carbon NanoTubes (SWCNTs), Highly Ordered Pyrolythic Graphite (HOPG) and Ir supported graphene sheet. The most relevant feature is the formation of a high BE component in Pd $3d_{5/2}$ spectrum, induced by those Pd atoms coordinated with surface defects. This interpretation has been suggested by the comparison of experimental results with the calculations on Pd/HOPG core level shifts for many different atomic species.

For Pd/SWCNTs we studied also the oxidation mechanisms, ranging on a wide spectrum of oxidation conditions. Our results confirm the presence of a 2D oxide
phase, as previously found on Pd single crystal, with some different behaviour induced by the reduced size of our particle.

Finally, the growth mechanisms and the chemical reactivity of Pt nanoclusters, supported on a MgO thin film has been studied by both energy and time resolved x-ray photoemission spectroscopy. The CO oxidation reaction has been investigated for different temperatures and different clusters’ size, resulting also in a deeper comprehension of the clusters’ morphology.
Abstract

L’attenzione rivolta dalla ricerca scientifica verso la catalisi eterogenea è alimentata dalla grande importanza che questa ha nell’industria chimica. I metalli di transizione sono tra i principali elementi che compongono i catalizzatori commerciali grazie alle loro ben note proprietà di reattività, che dipendono dalla loro struttura morfologica ed elettronica. Le proprietà catalitiche dei metalli di transizione possono essere ulteriormente migliorate riducendo la dimensione delle particelle sotto il nanometro oppure realizzando delle leghe tra differenti metalli di transizione.

Oggi è possibile prevedere la variazione delle proprietà chimiche superficiali in base alla posizione energetica del baricentro della banda d che è considerato uno dei più promettenti indicatori della reattività chimica. Questo parametro non è però facilmente accessibile sperimentalmente e viene tipicamente ricavato mediante simulazioni di calcolo. Un approccio promettente per stabilire una relazione tra le proprietà di struttura elettronica e la reattività chimica in modo sperimentale è basato sulla spettroscopia di fotoemissione a raggi X mediante sorgenti di radiazione di sincrotrone di terza generazione. L’alta risoluzione raggiunta negli ultimi decenni ha permesso l’identificazione negli spettri di fotoemissione dai livelli di core, dei contributi di fotoemissione originati dagli atomi di bulk e dagli atomi di superficie permettendo così la determinazione di quello che è comunemente chiamato Surface Core Level Shift (SCLS). Inoltre è stato dimostrato che il SCLS è un’ottima sonda della struttura elettronica superficiale dal momento che l’energia di legame dei livelli di core di un atomo dipende fortemente dall’ambiente chimico e strutturale in cui è immerso.

In questa tesi sono state investigate le variazioni indotte sulla struttura elettronica dalla riduzione della coordinazione, dalla compressione superficiale, dal diverso arrangiamento atomico e dall’interazione tra metalli differenti in una lega bimetallica per mezzo di esperimenti di spettroscopia di fotoemissione dai livelli di core ad alta risoluzione energetica, effettuati su sistemi di diversa complessità. Lo studio degli stati pseudomorfi del Pd sulla superficie (0001) del Ru è avvenuto tramite il confronto tra gli shift calcolati per i centroidi della banda d e gli shift dei livelli di core (CLS) misurati sperimentalmente per le stesse specie atomiche. Tale confronto ha rivelato una stretta relazione tra le due quantità. Per due delle strutture studiate (quelle composte rispettivamente da 1 e 2 ML di Pd sulla superficie di Ru) è stata testata anche la reattività chimica, esponendo queste superfici ad ossigeno molecolare. I risultati hanno confermato la stretta relazione tra shift dei centroidi della banda d, CLS e reattività chimica.

Un sistema più complesso, studiato successivamente, è quello composto da nanoclusters di Pd depositati su tre diversi supporti in carbonio: Single Walled Carbon NanoTubes (SWCNTs), Highly Ordered Pyrolythic Graphite (HOPG) e,
per finire, un singolo foglio di grafene cresciuto sulla superficie (111) dell’Ir. L’aspetto più rilevante di quest’esperimento è la formazione di una o più componenti ad alta BE nello spettro $3d_{5/2}$ del Pd, generata dagli atomi di Pd coordinati con i difetti superficiali. Tale interpretazione è stata suggerita dal confronto tra i dati sperimentali e le simulazioni sui livelli di core di una grande varietà di atomi di Pd non equivalenti.

Per quanto riguarda il Pd/SWCNTs è stato effettuato anche uno studio sui meccanismi di ossidazione, indagati su un ampio range di condizioni di pressione e temperatura. I risultati confermano la presenza di una fase bidimensionale di ossido, già riscontrata durante gli studi effettuati sul monocristallo di Pd. Ciononostante sono stati registrati svariati comportamenti peculiari ed originali, certamente indotti dalla ridotta dimensione delle particelle studiate.

In conclusione l’attenzione è stata rivolta alla crescita ed alla reattività catalitica dei cluster di Pt su film sottile di MgO. Tale sistema è stato studiato mediante spettroscopia ad alta risoluzione energetica (per la morfologia dei cluster) e temporale (per la reattività chimica). L’ossidazione del CO è stata studiata in funzione della temperatura del supporto e della dimensione dei cluster e ha fornito anche utili indicazioni sulla morfologia dei cluster stessi.
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A chemical reaction is a process in which one or more species, the reactants, undergo a transformation to become new species called products. Chemical reactions can be more or less energetically favourable, given different aspects of the reaction. A special class of chemical reactions are activated processes, for which the chemical transformation requires a supplied energy to start. When these reactions are used for industrial production of chemical species, the amount of supplied energy is an important parameter to take into account, and maybe a hard problem to solve.

It is well accepted that for many activated processes, the presence of certain chemical species favour the reactions, while remaining unchanged after the reaction: this phenomenon is called catalysis. Catalysts do not transform as reactants do, but participate in the chemical reaction, driving the process through a different, and often more complicated but energetically less expensive path.

Catalytic processes pervade worldwide industrial production, to the point that it is difficult to overstate their role into modern economies [1], and their importance therefore justifies the intense ongoing research efforts in this field. The daunting problems posed by trying to move towards a “sustainable growth”, are pressing towards more stringent requirements for less expensive and more efficient catalysts, and it is becoming even more important to devise new ways for improving and accelerating the process of new catalyst’s development [2].

Catalysis can be classified into three main classes. In bio-catalysis, reactions involve biological species and enzymes play the role of catalysts. In homogeneous catalysis the reactants and the catalyst are in the same physical state. In heterogeneous catalysis, catalysts are in solid state and favour the reactions of species in liquid or gas phase. This thesis deals with this latter class.

In recent decades heterogeneous catalysis has become the principal manner of production of many useful chemical substances, such as fuels, lubricants, refrigerants, polymers, drugs, and also plays a crucial role in air and water pollution reduction [3]. Despite its importance in so many different and fundamental processes, explanations of many of the phenomena involved in catalysis are still lacking, thus providing significant motivation for fundamental studies. In recent decades an impressive amount of effort towards understanding catalysis’ mechanisms has been done.

One of the most fundamental gaps in our understanding pertains to the complexity of systems involved. This complexity is related mainly in the size and the structure of real catalysts. They are usually powders, composed of transition metal (TM) nanoparticles supported by oxide layers. Atomic-scale characterization and
control of these kinds of systems is very difficult, thus hindering our ability to relate observed effects to nanoscopic details. For this reason, a different approach to catalysis has been chosen: the surface science approach.

Real catalysts’ properties arise from the interplay of many different effects: the size of active particles, the interaction between particles and support, the surface morphology of active materials. When characterizing a particular measurable quantity (for example, the chemical reactivity of the catalyst) is not possible to disentangle the different contributions in a direct way: in this correlation of causes lies the “complexity” of real catalysts. One possible way to overcome some of this complexity is to study so-called model systems. Model systems are physical systems that are simpler to understand than real catalysts, but that can be manipulated by experimentalists in order to determine which of their features is responsible for their chemical properties. Such simplicity typically can only be achieved under ultra-high vacuum (UHV) conditions: UHV allows atom by atom growth via physical vapour deposition, with a very low level of impurities or contaminants, allowing the system to retain the “model” design. The same conditions are used for performing measurements: in this way single steps of complex processes can be studied and we can follow a chemical reaction’s path in real time, with the capacity to distinguish on which kind of atom and in which conditions reactions occur.

The way in which we follow a chemical reaction is not a direct look on how, for example, a molecule approaches a metal surface towards a particular atom, dissociates, and so on. Some microscopy techniques can achieve this level of “direct looking”, but this thesis deals instead mainly with spectroscopic techniques.

Before the explanation of the main subject of this work, it is necessary to introduce the correlation between the chemical reactivity of TMs and physical properties of the systems we studied. In the last 15-20 years theoreticians concentrated their attention on the relation between chemical reactivity and electronic structure of TMs. The most important works in this field are those conducted by Hammer and Nørskov using Density Functional Theory (DFT) approach. A TM’s electronic structure is characterized by an $s$ and a $d$-band. They conclude that [5-9], being for all TMs the $s$-bands broad and half filled, the different behaviours of TMs arise mainly from their $d$-band structure. As shown in Fig. 1, the coupling between an adsorbate molecule’s and a TM’s electronic states can be seen as splitted in two successive moments. Adsorbate orbitals first couple with $s$-band, with a consequent energy shift and a broadening of the line. After this first “step”, the coupling with $d$-states gives rise to a two level situation, because of the narrow shape of the $d$-band, a solution similar to molecular orbitals (MO) with bonding and antibonding states. The situation is different than with molecules because solids do not possess discrete atomic orbitals that can be occupied or unoccupied, but rather an infinite sea of electrons: the occupancy of the antibonding states will depend on their energy with respect to the Fermi level ($\varepsilon_F$), as shown in Fig. 2. As previously stated, after $sp$ coupling, the atomic level of the adsorbate interacts with the $d$-band, which, being narrow, behaves like an atomic level. The MO-like situation manifests here with the antibonding level at an energy higher than $\varepsilon_F$, giving rise to a low antibonding contribution and, for this reason, to a strong adsorbate-metal interaction.
Hammer and Nørskov showed that the key role in determining the strength of the metal-adsorbate interaction is played by the position of the d-band centre of mass (with respect to $\varepsilon_F$). The closer the d-band centre ($\varepsilon_d$) is to $\varepsilon_F$, the less the antibonding level is occupied and the stronger the interaction, as is depicted in Fig. 2.

The relation between this electronic property and the chemical reactivity of TMs is illustrated in Fig. 3, where CO chemisorption energies on several different Pt surface sites are plotted versus calculated $\varepsilon_d$. An almost linear relation between these two quantities is observed, so the d-band center can be a reliable indicator of TMs’ chemical reactivity. In the second panel the H$_2$ BEs are related to surface d-band center for several subsurface Pt-3d-Pt(111) and surface 3d-Pt(111) structures [8]: the same linear trend is observed.

In summary, the particular catalytic properties of TMs originate from its very narrow valence d-band, which induces an enhancement of electronic DOS around
the Fermi level. For this reason a detailed study of electronic structure is the first fundamental step for understanding the catalytic behaviour of these materials. The present state of the art employs rare and precious metals (Rh, Pt, etc.) as the most useful catalysts for many useful chemical reactions. One of the main aims of

![Image of CO binding energy vs. d-band center](image1)

**Figure 3.** a) Calculated CO binding energy shown as a function of the d-band center for the adsorption site. The solid circles are for CO in the fixed adsorption geometry over the rigid surfaces. Also included as an open circle is the result for CO over Pt(211) vs. the d-band center at the step of bulk truncated Pt(211) [7]; b) DFT calculations correlating hydrogen binding energy to the surface d-band center for several subsurface Pt-3d-Pt(111) and surface 3d-Pt(111) structures [8].

materials science is to realize less-expensive catalysts; the solution to this problem of cost can be approached in two different manners. The first method aims to make sparing use of costly materials by designing new catalysts with only small amounts of precious metals. The second method aims to employ of altogether different (and less expensive) metals by tuning their size, geometrical arrangement and composition. As a representative case of the first approach is gold. Gold has long been known as having a chemical reactivity significantly lower than other TMs have. However, it has been found that when
dispersed as ultrafine particles and supported on metal oxides such as titania, it exhibits an extraordinarily high activity for low-temperature catalytic combustion.

**Figure 4.** CO oxidation rate (turnover frequency) at 300K as a function of the average size of the Au clusters supported on a high surface area TiO$_2$ [10].

Fig. 4 shows an example of how metal particle sizes can affect chemical activity of a material. The oxidation rate of CO strongly depends on particle size, with a maximum rate for clusters of about 3 nm [10]. This is an extraordinary finding that shows clearly how a metal particle’s dimensions can modify its properties. It is clear that the use of small amounts of precious metals is not only a way to spare expensive materials but, together with the correct choice of particle size, it is also a viable way to activate chemical properties of ordinarily inert materials. A more recent work [11] has demonstrated the role of atomic coordination respect to chemical reactivity.

**Fig. 5.** a) CO oxidation activity versus the gold particle size for a large variety of support materials [15]. b) Fraction of atoms at corners (red), edge (blue), and crystal faces (green) of the truncated octahedron displayed in the insert versus the particle diameter [15].
Chapter 1 - Introduction

In Fig. 5a CO oxidation activity is shown as a function of gold particle diameter on different oxide supports. Particles become active catalysts for this reaction for diameters of 5 nm and smaller, and have the highest activity with a 2 nm diameter. In the second panel we find the relative weight of different atomic sites as a function of particle size. As particle diameter decreases, the weight of corner atoms grows, with the same trend of the CO oxidation activity. Gold is thus an impressive example of the effect of particle size and furthermore of the influence of atomic coordination on chemical activity, however it is important to note that other TMs shows the same dependance.

As previously stated, the second method for producing cheaper catalysts is based in the use of less expensive metals. Alloying metals is a way to obtain systems with superior chemical activity than compared to their individual constituents. In [12-14] Near-Surface Alloys (NSAs), an alloy where the solute metal is present in higher concentration in host’s surface than in host’s bulk, are studied by DFT. In Fig. 6 we find calculated binding energies for hydrogen on different NSAs. In Fig. 7 hydrogen dissociation barriers calculated respect to the pure metal reference for both pure noble metals and various NSAs are shown. It is evident that NSAs with a hydrogen BE similar to those of Cu and Au have a lower hydrogen dissociation energy, that is to say that NSAs are energetically less expensive for energy production.

**Figure 6.** Hydrogen binding energies values on various close-packed surfaces. The reference energy corresponds to a gas-phase atomic hydrogen H(g) and a clean metal slab at infinite separation from one another. The horizontal dashed line at -2.28 eV corresponds to thermoneutral dissociation of H₂(g) [13].
Figure 7. Hydrogen dissociation energy as a function of the hydrogen binding energy on pure noble metals and NSAs surfaces. The energy reference for both $E_{TS}$ and hydrogen binding energy is a clean metal slab and a gas-phase hydrogen at infinite separation from one another [14].

While DFT calculations of the surface projected $\varepsilon_d$ are reasonably easy to perform (even for rather complex geometries, like e.g. stepped surfaces), the task of experimentally determining the surface $d$-band Density Of States (DOS) (using techniques such as Ultraviolet Photoelectron Spectroscopy) and disentangling it from the bulk DOS component, is extremely difficult because of band dispersion and overlapping contributions from species in different chemical and geometrical environment. A less direct but simpler alternative approach is to use X-ray Photoelectron Spectroscopy (XPS), the technique used in the present PhD project. It has been long known that electron Core Level (CL) Binding Energies (BE) provide an accurate local probe of the electronic structure changes of an atom in different chemical environments. The interpretation of CL shifts of the surface metal atoms based on the hypothesis of charge transfer has been examined by DFT calculations [11,12], and indicate that although CL shifts can give important information on surface reactivity changes, final state contributions can be significant, in particular for noble metals like Cu and Ag, where the low density of states at the Fermi level yields a rather inefficient screening of the core hole. Nevertheless, for a large number of TM systems (both, clean and adsorbate-covered), High Resolution X-ray PhotoEmission Spectroscopy (HRPES) experiments at modern synchrotron radiation facilities have shown a clear relationship between Surface Core Level Shifts (SCLS) changes, and the theoretically determined $\varepsilon_d$ shifts, thus indicating that in these cases the screening correction magnitude is rather small compared to the overall trend of initial state shifts. Because of these properties, the idea of using the changes of SCLS as an experimental descriptor of the trends in surface chemical reactivity has been put forward.
Since the 1970s HRPES technique has played a key role in elucidating the energetics, structure and kinetics of solid surfaces. There are many examples, regarding the interaction of atomic adsorbates, the role of surface defects, the thermal stability of solid surfaces and simple surface chemical reactions, that outline the potential of HRPES as a tool for determining electronic, geometrical and chemical properties of clean and adsorbate covered TMs solid surfaces. Here follows some example of how HRPES analysis can be used.

The ability to distinguish the adsorption sites of molecules chemisorbed on long range ordered solid surfaces dates back to the seventies, when the group of D. Menzel was the first to make quantitative use of adsorbate XPS on single crystal surfaces, to disentangle different C 1s core level components originating from CO molecules adsorbed on different sites on W(110) [17, 18]. After those pioneering experiments, XPS was extensively applied on transition metal surfaces to probe the molecular bonding configuration of adsorbed layers, such as CO on Ni(100) [19, 20], Pt(111) [21, 22], Pd(111) [23], Rh(111) [24, 25] and NO on Rh(110) [26] and Pt(111) [27].

A good example of this kind of analysis is the one found in [19]. Extensive real-time measurements of the Rh 3d core level have been performed in order to understand the evolution of the local configuration of the oxygen atoms, along with the variations of the electronic structure of the substrate Rh atoms. Fig. 8a shows a sequence of Rh 3d$^{5/2}$ spectra measured at different coverages during oxygen exposure at room temperature.

In Fig. 8b and c the multicomponent deconvolution is shown. The Rh$_0$ component originates from the clean surface atom, while the Rh$_1$ and Rh$_2$ peaks originate

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**Figure 8.** a) Evolution of the Rh 3d$^{5/2}$ core level spectra during oxygen uptake on Rh(100) ($T = 300$ K, $h\nu = 380$ eV), shown as sequence of spectra (bottom) and two-dimensional image (top). (b) Rh 3d$^{5/2}$ core level components as obtained from the fits of the spectra measured at oxygen coverage of 0, 0.18 and 0.37 ML. (c) Oxygen coverage dependent intensity of the three components, as obtained by fitting the spectra reported in (a).
from the surface Rh atoms single and double bonded to oxygen. The first derivative \( \frac{d\text{Rh}_0}{d\theta} \) calculated for low coverage is equal to \(-4.2\), thus indicating in a direct way that for each oxygen atom adsorbed on the surface, the intensity contribution of about four surface Rh atoms moves from \( \text{Rh}_0 \) to \( \text{Rh}_1 \): the initial adsorption site for oxygen is confirmed to be fourfold.

**Figure 9.** Upper panel: Rh 3d\( _{5/2} \) core level spectra corresponding to clean (left), 0.035 ML (central) and 0.095 ML (right) Rh covered surfaces. Lower panel: calculated CLSs versus: a) the coordination number \( n \); b) the effective coordination number \( n_e \).
In recent years HRPES encountered a great success in the analysis of more complex systems, like metal adsorbed atoms and dimers on metal surfaces [28-34]. A strong correlation between the CLSs, the effective coordination and the chemical reactivity of chemically inequivalent atomic species holds, the effective coordination being a way to weight each contribution to the coordination of an atom. In Fig. 9 an example of this correlation is depicted, for Rh adatoms and adsorbed dimers on Rh(100) and Rh(111) surfaces.

The main aim of this thesis work is to test the XPS reliability as a universal technique for the characterization of electronic properties and chemical reactivity for systems, formed by TMs deposition on various supports, with a wide range of complexity. As the support changes, many important differences occur in the TMs’ growth mechanism on the host material. In this way a variety of structures can arise, each with different chemical and geometrical environments. The control of the amount of TM and the choice of the support enable us to tune the weight of different contributions (system dimensionality, ligand effect, particle size) towards desirable electronic properties. An accurate CL analysis allows us to determine growth mechanisms and electronic structure changes from one system to another. In this way we may understand the relation between the interplay of structural and geometrical details and the change of electronic properties. Further to this analysis, with HRPES it also possible to evaluate changes which may have occurred in chemical reactivity in a more direct way. CL are indeed sensitive to the chemical environment and hence to the interaction of the system with gas phase chemical species.

Here follows a brief summary of this thesis contents.

Chapter 2 gives a brief overview on experimental technique used.

Chapter 3 is devoted to the bimetallic surface alloys, investigating the growth of Pd on a Ru(0001) support. The system is composed of several Pseudomorphic Overlayers (POs) and the role of strain and ligand effect are analyzed. For two of the nine structures obtained the reactivity with oxygen has been tested, to find a clear indication of the relationship between CL shifts and change of reactivity.

Chapter 4 is devoted to the Pd nanoclusters on carbon based supports (namely, single walled nanotubes (SWCNT), high-ordered pyrolytic graphite (HOPG) and graphene/ Ir(111)). With the help of theoretical calculations we have put forth a reliable interpretation of the clusters’ growth mechanism.

Chapter 5 is devoted to the oxidation of Pd nanoclusters on SWCNTs, yielding information on the thermal stability of oxide phases and on the size effects in the oxidation process of Pd structures.

Chapter 6 is devoted to the growth of Pt on the MgO/Ag(001) interface. For this system we also studied the catalytic behaviour of MgO supported Pt nanoclusters for the CO oxidation reaction.
Reference

Chapter 2 – Experimental approach

2

Experimental approach

The study of the interaction between electromagnetic radiation and solid state matter started at the end of the 19th century, with the experiments of H. Hertz [1] and W. Hallwacks [2]. These experiments demonstrated that when a UV radiation impinges on a solid, electrons are removed. This is the so-called photoelectric effect, but these pioneering studies did not provide a physical explanation for this effect, because of the lack of an adequate theoretical framework. The complete comprehension of this phenomenon was acquired only with the Einstein work, at the beginning of 1900. The photoelectric effect was explained as an implication of the quantization, just introduced by Planck, and for this fundamental contribution Einstein was awarded with the Nobel prize in the 1922.

In this thesis I used a particular photoemission-based technique, called X-ray Photoemission Spectroscopy (XPS). XPS makes use of the photoelectric effect induced by the exposure of a sample to X-rays, and yields copious information on the nature of solids at the atomic scale, affording detailed knowledge regarding the chemical bonds and, more in generally, the chemical environment of the solid’s surface.

The technique was introduced in the sixties by K. Siegbahn, who won the Nobel prize in 1981 for his efforts on this subject. At the outset of XPS the radiation sources relied on the electronic transition energies of certain materials, with typical emissions at X-ray wavelengths. These sources provided a very high energy, and allowed the detection of the deepest electronic levels of a solid’s atoms. These core levels preserve a highly atomic-like behavior, even if the atoms are embedded in the crystal lattice. This means that core levels are strongly localized and for this reason they produce photoemission spectra narrower than those produced by valence electrons, which are collected in a broad band.

Nowadays almost every element has been characterized by XPS [3] and has a well defined spectrum. By comparing a measured spectrum with these well known values one can determine the composition of a sample in which many chemical species are present, assuming as a first approximation that the photoemission intensity is proportional to the atomic density of the different elements.

The most appealing features of the XPS technique are its sensitivity to the chemical environment of the measured system and its great surface sensitivity. Depending on whether the emitted photoelectron comes from an atom which lies on a clean, atomically perfect sample surface, or from the sample bulk, or if it comes from a surface atom coordinated with an adsorbate, a difference in the
kinetic energy will be detected. This occurs because the local environment of the emitting atom modifies its electronic structure, not only within the valence band, but also within the core levels, inducing the so-called Core Level Shift (CLS).

The surface sensitivity is given by the small mean free path undergone by the photoelectrons. Even if the X-ray radiation can penetrate thousands of Ångströms into a solid, the emitted electrons experience a strong interaction with solid structure and the energy losses previously described make the photoelectrons exit with a lower BE or even remain inside the solid. As depicted in Fig 2.7, the mean free path of the emitted electron is different depending on the material we deal with and on the photoelectron kinetic energy, and is roughly described by the universal curve. The mean free path refers to is the distance an electron travels before undergoing an inelastic scattering event, and can be described by the following: the mean free path is \( \lambda_i(E) \) for an element \( i \) at a kinetic energy \( E \), then the intensity attenuation coefficient \( \alpha \) of the photoelectron flux through a layer of thickness \( d \) will be

\[
\alpha = e^{-d/\lambda_{el}(E)}
\]

In other words, the majority of photoelectrons are emitted from the first 5-10 atomic layers. If one requires a high surface sensitivity the photon energy should be chosen such as to obtain a kinetic energy range centered on the minimum of the universal curve.

In this chapter I will briefly summarize the theory of the photoemission process, the different contributions to the final core level lineshape and finally, the most important features of SuperESCA, the beamline of the Elettra synchrotron light laboratory where I performed most of the measurements described in this thesis.
2.1 The photoemission process

The photoemission mechanism is depicted in Fig. 2.1. The kinetic energy of the emitted electrons is given by the fundamental photoelectric effect equation

\[ E_{\text{kin}} = h\nu - BE - \Phi \]

where \( h\nu \) is the photon energy, \( BE \) is the binding energy of the excited electronic level and \( \Phi \) is the work function.

![Figure 2.1. Schematic energy diagram of the photoemission process.](image)

In this simplified representation of the photoemission process the correspondance between electronic energy levels and the measured photoemission spectrum is shown. The electrons originating from the region surrounding the Fermi level of the metal have the highest kinetic energies. According to equation 2.1, electrons with lower kinetic energies have higher binding energies. The Fermi level is the reference for the calibration of the BE scale.

The photoemission process can be depicted by a dividing into three steps:
- excitation of the bound electron;
- transport of the electron toward the sample surface;
- crossing of the surface/vacuum boundary.

The photoemission intensity arises from three contributions: the photoionization cross section, the probability of scattering events during the transport and the probability of crossing the surface potential barrier. Using the non-interacting electron approximation and according to energy and momentum conservations, two relations arise:

\[ E_{\text{kin}} = h\nu - \Phi - E_I \]
\[ k_{||} = \sqrt{2mE_{\text{kin}}\sin\theta} \]

where \( E_I \) is the ionization energy, \( k_{||} \) is the crystal momentum parallel to the surface and \( \theta \) is the polar emission angle (the normal component of momentum is not conserved in the crossing of the potential barrier at the surface). The ionization energy is defined as the difference between the total energy of an \( N \)-electron atomic system embedded in the crystal lattice and the same system with
N-1 electrons. The photoemission spectrum, within this approximation, would be therefore a series of Dirac delta functions, located close to the ionization energies of each of the excited electronic levels. The probability of the transition from the initial to the final state of the photoemission process $w_{i\rightarrow f}$ is provided by the Fermi’s golden rule:

$$w_{i\rightarrow f} = \frac{2\pi}{\hbar} | < \psi_f^N | H_{\text{int}} | \psi_i^N > |^2 \delta(E_{\text{kin}} + E_f^{N-1} - E_i^N - h\nu)$$

where $H_{\text{int}}$ is the Hamiltonian operator which describes the interaction between the photon and the electron system. The full Hamiltonian which describes the unperturbed atom has an N-electron wave functions as its eigenstates. One commonly uses the approximation that this wavefunction can be written as the product of the single-electron wave functions of the electron that will be removed during the photoemission process and the Slater determinant describing the (N-1)-electron wave function of the remaining electrons

$$\psi_i^N = \phi_i^j (\psi_i^{N-1 \ j})$$

where $\phi_i^j$ is the one-electron wave function of the jth electron, $\psi_i^{N-1 \ j}$ is the properly antisymmetrized (N-1)-electron wave function of the remaining electrons. The same can be written for the final-state wave function

$$\psi_f^N = \phi_f^j (\psi_f^{N-1 \ j})$$

where the function $\phi_f^j$ is describes the final state of the emitted electron. This decomposition of the N-electron wave function is helpful in the calculation of the transition probability. Substituting these products in the matrix element of Fermi’s golden rule we obtain

$$< \psi_f^N | H_{\text{int}} | \psi_i^N > = < \phi_f^j | H_{\text{int}} | \phi_i^j > < \psi_f^{N-1 \ j} | \psi_i^{N-1 \ j} >$$

The matrix element is easier to calculate because it is decomposed in two contributions: the one-electron transition matrix element and the overlap integral between initial and final (N-1)-electron states. Each of these two contributions influences the photoemission spectrum shape.

### 2.2 The core level lineshape

The matrix element can be calculated within the dipole approximation (for which $H_{\text{int}}$ is proportional to the dipole hamiltonian). It describes the overlap between the free electron wavefunction and the bound state of an electron perturbed by a photon. One can demonstrate that for this one-electron transition the energy-dependent probability density is given by

$$w(E) = \frac{\Gamma}{2\pi \left[ \left( \frac{\Gamma}{2} \right)^2 + (E - E_0)^2 \right]}$$
where $E_0$ is the binding energy of the excited electron and $\Gamma$ is the full-width at half maximum (FWHM) of the distribution. As we can see, the photoemission spectrum will not be a collection of Dirac functions: the mechanism of excitation and emission of the electron generates an intrinsic broadening of the energy distribution of photoelectrons, with a Lorentzian shape.

![Diagram of photoemission spectrum](image)

**Figure 2.2:** Schematic drawing of an XPS spectrum: the main line (adiabatic peak), and the shake-up and shake-off satellites are depicted [5].

The (N-1) electrons initial- and final-state wave functions are eigenstates of different Hamiltonians, because of the removal of one electron in the final state operator. For this reason, for a well defined initial state, many excited final states could exist, with non-zero transition probability. These excitations are generated by energy releases from the photon or from the photoelectron and are at the origin of the low-kinetic energy structures. In particular, as depicted in Fig. 2.2, if this energy release is directed to bound or unbound states different structures in the spectrum can arise, named shake-up and shake-off satellites respectively.

The effects considered until now give rise to spectra consisting of Lorentzian lineshapes, with features at higher BE, arising from energy losses. However, a real photoemission spectrum is more complex. Fig. 2.3 shows the main contributions to the core level lineshape. The intrinsic Lorentzian distribution of kinetic energy is influenced by many effects, such as the core-hole lifetime, crystal inhomogeneities, instrumental broadening, energy losses, and vibrational effects. In the following I will analyze each of these contributions to the formation of the photoemission line shape.
Figure 2.4: Comparison between the main contributions to the core level line shape for free molecules and solids [6].

**Core-hole lifetime.**
The core-hole lifetime depends on the different ways through which the hole is refilled. These mechanisms involve electrons with a binding energy lower than the core hole and can be radiative or not. The possible decay mechanisms, referring to the Fig. 2.5, are the following:

- **Auger process**: the core-hole in the K-shell is filled by an electron coming from a more external shell (L\(_1\)). The energy gain from the L\(_1\)-K transition induces the emission of another electron, from a less bounded electron (L\(_{2,3}\)). This process involve three electrons and leave the atom with two holes. The kinetic energy of the second photoemitted electron is given by the difference between the K-L\(_1\) energy gap and the BE of the L\(_{2,3}\) electron, thus it does not depend on the photon energy. For this reason, being fixed the kinetic energy, the BE of the Auger electron appers to change as photon energy does.

- **Coster-Kronig process**: the core-hole is filled by a less bounded electron coming from the same shell.

- **Fluorescence**: the refill of the core-hole by an external shell electron generates the emission of a photon with an energy equal to the K-L\(_1\) gap.

The time that the system employs to refill the core-hole influences the lineshape because of the time-energy uncertainty principle \(\Delta E\Delta t \geq h/2\), where \(\Delta E\) is \(\Gamma\), the Lorentzian FWHM.
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**Figure 2.5:** Most important decay channels: Auger process, Coster-Kronig process and fluorescence.

**Crystal inhomogeneities.**
When dealing with solid samples one must take into account the presence of inhomogeneities in the crystal lattice. The core level binding energy is the same for each atom in the solid if the crystal being studied has a perfect periodicity but in a real sample things work in a different way. Some atoms can have positions slightly different with respect to perfect crystal, because of the presence of defects such as steps, kinks or vacancies. If we assume the distribution of these defects to be random, photoelectrons originating from inequivalent atoms will have a Gaussian distribution in kinetic energy, centered on the kinetic energy related to the perfect crystal atom. As we will see, this effect strongly occurs in the study of supported nanoclusters. In those systems the reduced size and the disordered structure of the particles causes the presence of many inequivalent atomic species and, by the way, the spreading of the signal in may unresolved components, perceived by the data analysis as Gaussian broadening.

**Vibrational effects.**
This is another important source of the lineshape broadening. In some cases the transition from initial to final state can induce the variation of inter-atomic distance or in the adiabatic potentials, activating vibrational modes. The possible configurations are schematically depicted in Fig. 2.6, assuming that the initial state always lies at the vibrational ground state. In the panel a) there is no vibrational state transition because the overlap between the two electronic wavefunctions is maximized by the transition \((\nu_i=0 \rightarrow \nu_f=0)\).

With the exception of the vibrational ground state, well populated in the central zone, all other vibrational states are more populated at the boundaries. For this reason, in the panel b) the most favoured transition will be \((\nu_i=0 \rightarrow \nu_f=1)\) and \((\nu_i=0 \rightarrow \nu_f=3)\), whereas in the
panel c) describes a mid-way situation, in which the main contributions come from \((\nu_i=0 \rightarrow \nu_f=0)\) and \((\nu_i=0 \rightarrow \nu_f=1)\), with an asymmetric shape of the vibrational profile. This analysis point out the occurrence of the lineshape broadening induced by vibrational effects for the molecules and is well applicable to the case of surface adsorbates. Nonetheless, the same effect occurs in solid state sample, because of the coupling of the photoelectrons with the phonons, with an influence on the lineshape that becomes stronger as the temperature increases, and with different trends for the bulk and the surface contribution, as depicted in Fig. 2.7 for the Ir(111) surface we measured [7].

**Figure 2.7.** Square of the total Gaussian width vs temperature for Ir4f7/2 bulk (black) and surface (blue) components. Note the different slope of the surface line.[7]

**Instrumental broadening**

The line broadening due to the experimental resolution that originates principally from the monochromator and electron analyzer is usually described by a Gaussian distribution. The experimental apparatus I used will be described more in detail below, but we point out here that the overall effects to the core level lineshape due to temperature, phonon scattering, inhomogeneities and experimental resolution are described by means of a Gaussian function.
**Energy losses.**

In addition to the already described intrinsic energy losses (*shake-up* and *shake-off* processes), the photoelectron can undergo extrinsic losses, during its escape path through the solid. These losses are consequences of the creation of collective charge oscillations called plasmons, or of electron-hole pairs in the vicinity of the Fermi level. This latter effect manifests as an asymmetry in the core level lineshape.

Finally, inelastic scattering events undergone by the photoelectron produce a considerable number of low energy secondary electrons, Auger electrons and photons. The first are responsible for the characteristic background of XPS spectra, which changes as a function of the photoelectron kinetic energy. This makes it important to choose the photon energy $\hbar \nu$ in such a way that the ejected electron will have a sufficiently high kinetic energy as to minimize the secondary electron contribution, or at least low enough to obtain a good signal-to-noise ratio.

Collecting all of the effects described above, Doniach and Sunjic [8] proposed the following parametrization of the core level lineshape in photoemission spectra:

$$I_{DS}(E_{\text{kin}}) = I_0 \frac{\Gamma_E (1 - \alpha)}\left[ (E_0 - E_{\text{kin}})^2 + \frac{\Gamma_E^2}{4} \right]^{(1-\alpha)/2} \zeta(E_{\text{kin}})$$

being

$$\zeta(E_{\text{kin}}) = \cos \left[ \frac{1}{2} \pi \alpha + (1 - \alpha) \tan^{-1} \left( 2 \frac{(E_0 - E_{\text{kin}})}{\Gamma} \right) \right]$$

where $\alpha$ is the asymmetry parameter, $\Gamma$ is the lorentzian FWHM, $E_0$ is the position of the maximum intensity and $\Gamma_E$ is the Gamma function

$$\Gamma_E(x) = \int_0^\infty t^{x-1} e^{-t} \, dt$$

The Doniach-Sunjic function is further convolved with a Gaussian that describes all the symmetric broadening contributions described above (vibration, phonon, experimental resolution, etc).

**2.3 The SuperESCA beamline of Elettra.**

A great advance in XPS technique came from the use of synchrotron radiation. When a charged particle, traveling at a speed approaching the light speed, undergoes an acceleration, it emits electromagnetic radiation in a very narrow cone and in a direction tangential to its motion, as depicted in Fig. 2.8. The electromagnetic radiation produced in this way has many important qualities:

- **brilliance** (defined as the number of photons for unit time and solid angle): it is some orders of magnitude higher than the one obtained conventional sources.
• *emission spectrum*: it goes from infrared to hard X-rays. One can choose the right photon energy by a monochromator, while preserving a high intensity because of the overall high brilliance.

• *polarization*: high degree of polarization, which can be eventually changed from linear to circular using different insertion devices.

• *time resolution*: radiation is emitted in short pulses with high frequency (MHz).

![Figure 2.8. Radiation produced by relativistic electron in motion along a circular trajectory.](image)

When used in photoemission experiments, these features allow for shorter data acquisition times and higher energy resolution, and thus synchrotron radiation sources are very appealing. The reduced acquisition time, combined with the capability of the SuperESCA to collect data in-situ while dosing, make it possible to measure the evolution of core levels during a reaction.

All the measurements of this PhD thesis work have been performed at the SuperESCA beamline at Elettra, the third generation synchrotron light laboratory in Trieste. This experimental station is composed by several parts. Starting from the storage ring side we can find:

• **The undulator**: it is characterized by a 56 mm period and has a minimum gap of 19 mm. Furthermore it is divided into three sections of 81 periods and can generate photons with energy ranging from 85(120) to 1500(2100) eV, depending on the ring electrons’ energy 2(2.4) GeV. The wavelength can be tuned by modifying the magnetic field generated by the undulator by changing the gap between magnets.

• **The monochromator**: the photons produced by the undulator are collected by a cylindrical pre-focusing mirror and then directed on the movable diffraction grating, which allows to select the photon energy in a range from 85 eV to 1000 eV, with a photon flux ranging from $10^9$ to $10^{12}$ photons/s. After this step the photons are focalised by two elissoidal
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mirrors. The highest E/ΔE resolving power one can reach is about $10^4$, at 400 eV photon energy and with a photon flux of about $10^{11}$ photons/s.

- The experimental station: it is composed by two chambers, separated by a valve. The upper part is the preparation chamber, where all the high pressure operations are performed (sample preparation by sputtering and annealing, gas exposure at high pressure, metal deposition, thin film preparation, etc.). This valve aims to preserve a clean, contaminants free environment in the measurement chamber, where the photons arrive on the sample. The latter can be moved from one chamber to the other, close to the different tools, by means of a manipulator with 5 degrees of freedom with heating and liquid nitrogen cooling capabilities.

When the sample is aligned with photon beam the photoemission occurs and the photoelectrons are collected by an electrostatic lenses system and guided towards the entrance slit of one of the most important parts in the SuperESCA beamline: the electron energy analyzer. The high energy and time resolution are accessible not only by the use of synchrotron radiation but also by recent improvements in analyzer technology.

The SPECS Phoibos electron energy analyzer, depicted in Fig. 2.9, is composed by a hemispherical capacitor, with 150 mm mean radius $R_0$. Applying a different potential to each hemisphere ($V_1$ and $V_2$), and being $R_1$ and $R_2$ their radii, the potential on the hemispherical surface with the mean radius will be

$$V_0 = \frac{V_1 R_1 + V_2 R_2}{R_1 + R_2}$$

In this way, only the electrons with a kinetic energy equal to $eV_0 = E_0$ will complete the path through the capacitor, to be detected by the electron counter, positioned after the exit slit.

**Figure 2.9.** Diagram of the hemispherical electron energy analyzer. The three trajectories depicted are what expected for electron with a kinetic energy smaller, equal and higher than the pass energy $E_0$. 

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The energy $E_0$ is called pass energy and has a key role in the energy resolution of the measurement. The entrance slit impose to the analyzer an angular acceptance with respect to the trajectory tangent to the mean radius path. If $\alpha_{\text{max}}$ is the largest entrance angle of an electron that complete the full path, the energy resolution can be estimated as

$$\Delta E \approx \frac{w}{2R_0} + \frac{\left(\alpha_{\text{max}}\right)^2}{4} E_0$$

where $w$ is the average between the entrance and the exit slit width (in our setup practically only the entrance slit has an influence on energy resolution). The optimal combination of these geometrical and working parameters is not a trivial argument. Decreasing the pass energy lowers the electron energy spread but implies also the lost of many photoelectrons that causes a decrease in the signal/noise ratio. The increase of the mean radius improve the energy resolution, but also impose an hard work in vacuum generation, because of the increase of the volume, and other problems connected with accurate machining of large hemispheres.

The SuperESCA electron energy analyzer works at a fixed pass energy, so we have to point out how photoelectrons with different kinetic energy could reach the the electron counter. As we said just before, the photoelectrons emitted by the sample arrive to hemispherical capacitor after a short path inside an electrostatic lenses system, a complex tool with two fundamental aims. The first is to reduce the angular spread of the photoelectrons, concentrating them on the entrance slit, for preserving a large signal. The second is to lower the kinetic energy of the emitted electrons until they reach the pass energy value.

During the photoemission process, photoelectrons with KE ranging from zero to $KE_{\text{max}} = h\nu - \Phi$ are all emitted simultaneously from the sample. Before beginning a measurement, the BE range of interest is chosen, together with the energy step size in each sweep. At every measurement step the potentials applied to the lenses are set to a specific value, in such a manner as to decelerate all photoelectrons by a fixed amount. Thus, at every energy step only those photoelectrons whose decelerated KE is close to the PE value are able to traverse the entire path through the hemispherical analyzer, where the number of photoelectrons is counted by the detector. In this way, ranging the lenses potential on a gap depending on the BE range choice, the spectrum arises from the collection of every single sweep.

The detector has a great influence in the energy and time resolution of an electron energy analyzer and SuperESCA has one of the most refined instruments available for this kind of measurement. Its working principle is depicted in Fig. 2.10.

The electron beam, impinging on the the multichannelplate (MCP), is multiplied and goes to hit the cross delay anode detector (CDAD). This zone is designed in such a way to generate two signals with opposite direction as the electron beam arrives. These two signals are first amplified and then converted to digital format by the constant fraction discriminators (CFD). Their output, a highly precise time detection of the signal peak arrival, is finally processed by the time to digital converter (TDC) and transformed in a digital value of the delay between the two orginal signals. This delay becomes a refined spatial information of the point in
Figure 2.10. Detector’s working principle. The time delay between the two signals originated by the CDAD are finally converted in a spatial position of the impinging electron beam, and so in the energetic distribution inside the single energy channel.

which the two signals originated and from this spatial determination the energy of the photoelectron is extrapolated.
The calibration of this system has been a very hard work, because of many factors (the finite dimension of electron beam impinging on the CDAD, the secondary electron noise produced by the MCP, the occurrence of non-linear effects, etc.) but gives both energy (high precision time to spatial to energy determination) and time (very short acquisition periods) resolutions, that allow to perform new kind of measurements, as the direct study of a chemical reaction through the real-time observation of core levels evolution.
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Reference


As previously stated, one way to tune an object’s electronic properties is by controlling its structural and geometrical features. Of these features, the most important are the dimensionality and the size of the structures and the choice of materials involved. Bimetallic surface alloys, specifically pseudomorphic overlayers, are a very good example of the model systems described in the introduction.

In surface science and UHV approaches, bimetallic surface alloys are obtained by physical vapour deposition (PVD) of a metal (D) on a well ordered surface of a host metal (H). In alloying two different metals, many different behaviours can arise, depending on a physical quantity called the segregation energy [1]. This is defined as the difference between total energies of two systems: a D atom on the surface of a H substrate and a D atom in the interior (the bulk) of a H substrate. In other words, we could define segregation energy as the energetic cost of a D metal impurity transfer from the bulk to the surface of the H metal. Depending on the sign and the value of this quantity, D metal might favour lying on the H surface, or instead favour diffusion into the H bulk. For the formation of bimetallic surface alloys it is necessary to choose metal couples with a high segregation energy, where the positive sign indicates the trend to remain on H surface for the D metal. For low values of segregation energy we might find different intermediate behaviours, such as surface intermixing (the presence, on the first atomic layer of both D and H atoms), or subsurface alloying, for which D metal do not remain on the topmost layer but rather beneath the first layers of H surface.

**Figure 1. Schematic diagram of the three growth modes usually observed for metal overlayers.**
For D-H couples for which segregation energy is large and positive, D metal will grow on H in several different ways. Three principal growth mechanisms [2] (summarized in Fig.1) have been distinguished: Frank-van der Merwe (FW) mode, known also as layer-by-layer mechanism, Stransky-Krastanov (SK) mode, where after the completion of the first layer, subsequent D metal grows in islands, and Volmer-Weber (VW) mode, for which D grows by formation of three dimensional island with no wetting layer. These different mechanisms arise from thermodynamic arguments (mainly the surface free energies of D, H and D-H interface) and the deposition process can be divided into three successive steps:

- **Initial nucleation**
  Individual D atoms from the vapour phase hit the H surface. Depending on D mobility on H (given by the substrate temperature and interaction), D atoms can diffuse freely on the H surface until they start a nucleation process, having met a substrate defect (such as the step between two terraces), an existing cluster or, more in general, a nucleation site.

- **Mono and bi-dimensional structures growth**
  In the FV and SK growth modes, D metal can grow at submonolayer coverages forming nanostructures like 1D chains or 2D islands. Even if thermodynamic arguments assert that 1D crystals of infinite length cannot exist in an isotropic environment, a single crystal substrate can have an anisotropic atomic distribution and, therefore, stabilize anisotropic structures.

- **Multi-layer growth**
  In the first two mechanisms, the 3D growth starts after the completion of the first adlayer. The term "pseudomorphic growth" refers to a situation where the first metal overlayer adopts a lattice constant which differs from its bulk value but which matches with the H metal surface lattice. In general, only the first layer grows pseudomorphically, while subsequent layers tend to manifest lattice constants that are closer to the crystal structure of the bulk admetal.

Heterometallic bond studies in bimetallic surface alloys afford a more accurate understanding of CLSs causes. The electrostatic perturbation, arising from the rearrangement of valence band, is not caused only by charge transfer. When two different metals form a bond, a hybridization of valence atomic orbitals occurs and induces a perturbation also on CLs. All events related to the bond between different metals is known as ligand effect. Moreover, the adlayer interatomic distances are not the ones we find in the monocrystal surface but are influenced by the atomic step of substrate surface. This effect, called strain, can be compressive or distensive, and in both cases generates a modification of valence orbitals and consequently in CLs. As we will see, bimetallic surface alloys could be useful tools for disentangling these two effects’ contributions to electronic structure modification.

The following is devoted to the study of Pd deposition on Ru(0001) surface. The first part describes the characterization of the growth mechanism, combining SPA-LEED and HRPES analysis. Next is a comparison of theoretical calculation on d-band center shifts, performed by the group of prof. Dario Alfè (University College, London), with CLS data. At the end of the chapter we analyze data from Pd/Ru interaction with oxygen.
3.1 Pd/Ru(001)

The characterization the Pd growth process was done in a ultra-high-vacuum (UHV) chamber equipped with an ion gun, a manipulator with four degrees of freedom with heating and cooling capabilities, and a Pd evaporator. The Ru crystal was cleaned by cycles of Ar⁺ sputtering (10 μA·cm⁻²), annealing to 1570 K, and O₂ treatment at 5 x 10⁻⁷ mbar in the temperature range 1000-1200 K, for removing the residual carbon. A final annealing to 1570 K was done to induce oxygen desorption. After this procedure, the sample showed a sharp (1x1) Low Energy Electron Diffraction (LEED) pattern with low background, and flat terraces about 500 Å wide, as results from the profile analysis of the LEED spots. The Pd evaporator consists of a 0.25 mm diameter high-purity Pd wire, which can be resistively heated. The evaporation filament is housed in a tantalum cylinder, with an opening of about 20 mm diameter at the front face for depositing the metal directly onto the Ru substrate, while preventing Pd evaporation onto UHV system components. The metal source was gradually heated and then held at the evaporation temperature for a fixed amount of time. The pressure in the UHV systems was always kept below 4x10⁻¹⁰ mbar to prevent the adsorption of background impurities on the bimetallic surface. In order to characterize the growth process, high k-resolution electron diffraction data were taken using an Omicron Spot Profile Analysis LEED. By means of this instrument, which has a transfer width of ~1000 Å, high-quality reciprocal space maps, i.e. two dimensional scans, and the zero-order diffraction beam spot profiles were acquired at fixed energies. Reproducible deposition of impurity free metal overlayers was routinely achieved. The LEED beam profiles at different Pd coverage were acquired at room temperature.

![Figure 2. SPA-LEED out-of-phase spectra of zero order diffraction spot. For two different Pd amounts (one twice respect to the other) we find single and multi-component spectra.](image-url)
The characterization of the Pd growth mode and the coverage determination were performed in out-of-phase Bragg condition of the zero-order diffraction beam, corresponding to an electron energy of 85 eV. The specular diffraction spot intensity modulation and its line profile changes were measured to investigate the thermodynamic growth mechanism [3]. The periodic modulation of the diffraction intensity and the absence of extra-tails at the zero order diffraction spot sides are indicative of a Frank-van der Merwe hetero-epitaxial growth, while the appearance of extra peaks between maxima is linked to the formation of Pd islands with a characteristic correlation length (Fig. 2). Pd deposition at T=320 K with a flux of about 0.9 ML/minute (followed by subsequent annealing at 670 K), resulted in a layer-by-layer growth up to 2 ML, as already reported in previous investigations [4]. During formation of the third layer, a slight disordering takes place with the fourth layer starting to form before the completion of the third. Having determined the optimal evaporation conditions (filament current, evaporation time, substrate temperature and post deposition annealing temperature) for layer-by-layer growth of Pd on Ru(0001) were determined, the evaporator was moved to the SuperESCA beamline for the HRPES measurements [5].

The SuperESCA experimental station has been described in the previous chapter. The base pressure during measurements was $1 \times 10^{-10}$ mbar. The Pd and Ru $3d_{5/2}$ photoemission measurements were performed at normal photoelectron emission conditions with the sample at room temperature and a photon energy of 410 eV. The overall energy resolution (electron energy analyser and x-ray monochromator) was 40 meV for both Pd and Ru $3d_{5/2}$ core level spectra. The electron binding energies are referred to the Fermi energy position, measured under the same experimental conditions (photon energy, analyzer setup, and surface temperature). HRPES measurements in the C 1s, S 2p, and O 1s core level regions, confirmed the absence of contaminants. All the photoemission data have been fitted by a convolution of a Doniach-Sunjic (DS) function and a Gaussian, which accounts, as we have seen, for the phonon broadening and the contribution of the instrumental resolution. A linear background was also subtracted. The DS profile contains a Lorentzian distribution (described by the $\Gamma$ parameter) arising from the finite core hole lifetime, and an asymmetry parameter $\alpha$ to account for electron-hole pairs excitation at the Fermi level.

Figures 3 and 4 show series of Ru $3d_{5/2}$ and Pd $3d_{5/2}$ CL spectra, respectively, for different Pd deposition times, up to completion of three Pd MLs. As previously reported [6,7], the Ru $3d_{5/2}$ CL spectrum of the clean surface (before starting Pd deposition), consists of three components highlighted in Fig. 3: a peak centered at 279.70±0.02 eV, originating from Ru atoms of the first layer (Ru$_1$ – dark blue); a peak at 280.21±0.02 eV, due to second layer atoms (Ru$_2$ - light grey) and, finally, a third component at 280.08±0.02 eV, due to deeper, bulk layers (Ru$_3$ - dark grey). The best-fit parameter values are 180±20 meV for the Lorentzian width, 0.08±0.02 for the asymmetry parameter and 120±20 meV for the Gaussian width of the bulk component, while the first- and the second-layer Gaussian widths were 170 meV and 90 meV respectively, in good agreement with the values found in previous determinations. All the fits gave very small and structureless residuals, proving the accuracy of the method.
Figure 3. Series of high-energy resolution Ru 3d$_{5/2}$ core level spectra collected at $T=300$ K after different Pd deposition times. The solid lines superimposed to the experimental data (open circles) are the result of the final fits; the colored curves correspond to the different Ru components. The individual components are plotted after linear background removal.
Figure 4. Series of high-energy resolution Pd 3d_{5/2} core level spectra collected at T=300 K after different Pd deposition times. The solid lines superimposed to the experimental data (open circles) are the result of the final fits; the colored curves correspond to the different Ru components. The individual components are plotted after linear background removal.
Upon deposition of sub-monolayer quantities of Pd, (exposure times of 30 s and 60 s), a single component grows in the Pd 3d$_{5/2}$ spectral region, at a BE of 335.15±0.02 eV (Pd$_1$ - orange curve, Fig. 4). In the corresponding Ru 3d$_{5/2}$ spectra, the Ru$_1$ component intensity drops markedly, and a new peak (Ru$_4$ - light blue, Fig. 3) with a SCLS of -180 meV appears. The progressive growth of this component in the 30 s and 60 s spectra, is paralleled by a decrease of the Ru$_1$ peak intensity (-40% and -75%, respectively). This is expected, since the fraction of Ru ‘clean’ surface atoms (i.e. not coordinated to adsorbed Pd atoms) decreases progressively as the Pd coverage increases. At the same time, the signal originating from Ru bulk and Ru second layer atoms is progressively attenuated by the growing Pd overlayer.

At 80 s and 120 s Pd deposition times (corresponding, as determined by SPA-LEED measurements, to intermediate coverages between 1 and 2 ML), the Ru$_1$ signal vanishes, while the corresponding Pd 3d$_{5/2}$ spectrum undergoes large modifications. A tail at higher BE and a shoulder at lower BE with respect the Pd$_1$ component appear, and the fit requires just two extra components, shifted by +220±40 meV (Pd$_3$ – yellow curve, Fig. 4) and -370±40 meV (Pd$_2$ – orange curve, Fig. 4), with respect to the Pd$_1$ component, respectively. For a Pd deposition time of 135 s (corresponding to ~2 ML coverage) the Pd$_1$ population has vanished, and the Pd 3d$_{5/2}$ spectrum can be described by using only the Pd$_2$ and Pd$_3$ peaks. Two components, shifted by 530 meV, in the Pd 3d$_{5/2}$ spectrum above 1 ML Pd coverage were already reported by Andersen et al. [8]; and the presence of a third component was most probably hidden by the lower experimental resolution of their measurements.

At deposition times exceeding 135 s, the spectrum undergoes further modifications: the spectral minimum slowly starts to be filled by a new component (Pd$_4$ – brown curve, Fig. 4) at a BE of 335.04±0.02 eV. Although its BE is very similar, this new peak has a different physical origin than Pd$_1$. As it will be shown below, it arises from second layer atoms in a 3 ML Pd film. The lowest BE component seems to be moderately sensitive to this further Pd thickness increase: on increasing the coverage from 2 to 3 Pd MLs, it appears to shift only by about 40 meV towards lower BE. At these Pd coverages, all the Ru 3d$_{5/2}$ spectral components are still present in the spectra, but with progressively decreasing intensity.

Fig. 5 shows a comparison of the Ru 3d$_{5/2}$ Core Level shifts measured after 30 s of Pd evaporation time with the calculated d-band center shifts $\varepsilon_d$. Panel (a) shows schematically the $\varepsilon_d$ values (calculated with respect to the clean Ru surface $\varepsilon_d$ value), while panel (b) shows the corresponding CL BEs. By choosing the first layer (surface) BE as the origin of the shifts, the second layer’s CL shift is 460 meV, while the third layer atoms’ (representative of bulk atoms) shift is 370 meV. As previously stated, the Ru spectrum presents an extra component with respect to the clean surface (light blue in Fig. 5b, at a shift of 200 meV), originating from the Ru surface atoms on which Pd atoms have adsorbed (see inset). The corresponding projected d-band center shift is 270 meV. The overall correspondence is satisfactory and confirms that the contribution of screening (always below 100 meV for the clean Ru(0001) surface [6]) does not obscure the initial state trend. Final state corrections, however, would be needed for obtaining an accurate quantitative agreement with the measured data.
In the following we discuss in detail the Pd spectra, since their behavior is more closely connected to the chemical significance of our results. As already described in Section 3, after 30 s of Pd deposition (corresponding to about 0.4 Pd ML), a single isolated peak appears at 335.15 eV BE. This feature grows linearly with Pd deposition time. The 3ds/2 Pd CL for a clean Pd(111) surface has been previously measured at a BE of 334.60 eV [9], so we conclude that the adsorption process of Pd adatoms on a Ru(0001) surface causes a Pd 3ds/2 BE change of 550 meV. Since the atomic coordination number for both surfaces (Ru(0001) and Pd(111)) is the same (i.e. 9), the shift of 550 meV originates mainly from a combination of ligand and stress effects. Indeed the Ru-Ru interatomic distance is known to be slightly smaller (~1.8%) than the Pd-Pd distance.

Our DFT calculations for a clean Pd surface layer (of Pd metal), and for a Pd PO on Ru(0001), give \( \varepsilon_d \) values of 1.63 eV and 2.12 eV respectively. These values are schematically compared with Pd 3ds/2 BE changes in Figure 6a and 6b. According to the \( d \)-band model of chemical reactivity, such large energy downshift (\( \Delta \varepsilon_d \sim -30\% \)) should correspond to a dramatic reduction of adsorbate binding energies. Indeed Behm and coworkers [10] find a 30% reduction of deuterium adsorption energy on a Pd ML deposited on Ru(0001), with respect to the adsorption energy on a Pd(111) surface. Moreover, Pallassana et al. reported a significant larger binding strength of ethylene on Pd(111) (~62 kJ/mol) when compared with Pd.
monolayer on Ru(0001) (-31 kJ/mol) [11]. Panel d in Fig. 6 shows the position of the Pd $3d_{5/2}$ spectral components after 120 s Pd deposition time (corresponding to 1.8 Pd MLs). In principle, after completion of 2 Pd MLs, 2 peaks should be present in our spectra (originating respectively from the outermost surface layer and from the interface layer with the Ru substrate).

Figure 6. Comparison of experimental binding energy of Pd $3d_{5/2}$ Core Level components, and theoretical layer-projected d-band centers, for Pd$_n$ (0≤$n$≤3) overlayers deposited on Ru(0001). Shift of the Pd d-band center and $3d_{5/2}$ CL for (a, b) 1 Pd pseudomorphic overlayer; (c, d) Pd$_n$ layers with 1≤$n$≤2; (e, f) Pd$_n$ layers with $n$=3. The insets on the left show schematically the physical systems for which the comparisons are done. Both CL and d-band center shifts are referred to the clean Pd(111) surface CL and d-band center.
Chapter 3 – Pd/Ru(001) pseudomorphic overlayers

Figure 7. Relationship between Pd 3d$_{5/2}$ Core Level components, arising from Pd overlayers and corresponding DFT calculated d-band centers. The circles in the figure are color coded according to the insets in the upper left and lower right of the figure. The relationship is strikingly linear, showing that final state effects do not obscure the Core Level Shift trends, as indicators of chemical reactivity.

The surface CL components of our HRPES data reflect this situation: two major peaks are found at 770 and 180 meV with respect to the pure Pd surface peak. In addition, the spectrum at this coverage shows a third (weak) component, at a 550 meV energy shift. This component is at the same energy as the Pd peak in Fig. 6a and we therefore interpret it as originating from Pd atoms adsorbed on Ru, and not yet covered by the second Pd layer (which is still incomplete). According to our DFT calculations, the energy center of the d-band is found at 2.40 eV, while the surface-atoms projected ε$_d$ lies at 1.76 eV. The shifts of ε$_d$ with respect to a pure Pd surface layer are therefore 770 meV and 130 meV, respectively (see panel c in Fig. 6). According to the d-band model, this means that the surface chemical reactivity has now substantially increased with respect to the situation of a single Pd ML adsorbed on Ru, but it is still lower than in the case of a pure Pd surface. Finally, panels e and f in Fig. 6 depict the situation after 200 s of Pd deposition, when nearly 3 MLs of Pd have been deposited. At 3 ML of Pd coverage on Ru, we expect three peaks to appear in the Pd 3d$_{5/2}$ spectrum (one for each layer), and this is indeed what is observed. Furthermore the theoretical DFT results give three different E$_d$ values at 80, 440 and 760 meV with respect to the ε$_d$ of the Pd clean surface first layer.

In summary, the CL shift of the topmost Pd layer is 550 meV when only 1 ML is present, 180 meV when 2 MLs have been deposited, and finally 150 meV when there are 3 Pd ML. The very small difference in the shifts between the 2 ML and 3 ML cases shows that the ligand effect originating from the Ru interface does not contribute significantly beyond the third Pd atomic layer. The remaining shift therefore can originate only from the strain caused by the Pd layer maintaining the Ru lattice parameter. We conclude that the CL BE analysis allows a proper distinction between ligand and strain effect contributions. In the case of the Pd/Ru(0001) we find that the ligand effect contribution is twice as large as the
stress effect. A compendium of our experimental and theoretical results for 1, 2 and 3 Pd MLs is shown in Fig. 7. It is immediately apparent that a very clear linear relationship (linear correlation coefficient 0.99±0.01) between the measured Surface Core Level binding energies, and the calculated d-band centers exists. We argue therefore that, although measured CL BEs are definitely affected by final state contributions intrinsic to the photoemission process, these contributions do not significantly alter the overall trend for Pd overlayers on the Ru(0001) system. Our results confirm that, also for the POs, SCLS changes are a useful experimental descriptor of the projected d-band center of transition metals’ and therefore, according to the d-band model, of TMs’ chemical reactivity.

3.2 Pd/Ru(0001) oxygen chemisorption

After having described the Pd growth on Ru(0001) surface we attempted to study the chemical reactivity of selected structures among those prepared in the first part of the experiment. We choose to expose 1 and 2 Pd overlayers systems to molecular oxygen, with doses between 60 and 70 Langmuirs. The choice of these specific structures has been kept because of the strong differences arising in Pd 3d_{5/2} CLs of the different surfaces. Between 2 and 3 Pd MLs small changes occur (about 30 meV) whereas between 1 and 2 Pd MLs a shift of 370 meV has been measured. In this way we expect to find a difference in chemical reactivities, to relate to the high CLS between the two structures.

During oxygen exposure the sample was held at room temperature and the oxygen pressure was been raised from 10^{-9} to 10^{-7} mbar, as recorded during the experiment. The electron analyzer was not used in high energy resolution but rather in time resolved mode. A Pd 3d_{5/2} spectrum was collected every 20 seconds: in this way, thanks also to the low pressures of oxygen exposure, we were able to measure the evolution of lineshape in real time, recording the modification of the bimetallic system due to oxygen chemisorption. In Fig. 8a we show the full sequence of spectra for the 1 Pd ML system and it is clear that no changes occur in the CL spectrum. In Fig.8b we show only the first and the last spectra of the full series, to underline the absence of modifications in the core level spectrum line shape and intensity. In full agreement with these measurement is the LEED pattern, that show a sharp (1x1) periodicity with no traces of adsorbates.

It has long been known [12] that if the clean Pd(111) surface is exposed at room temperature to 20 L of O_2, the (2x2)-O with an oxygen coverage of 0.25 ML is formed. However, dosing 60 L on the Pd surface in the single overlayer system we find a completely clean Pd pseudomorphic surface. The HRPES data reported in Fig. 6a are in some agreement with this observation, because of the 550 meV shift of 1 Pd ML CL respect to the Pd(111) surface CL.

In [13], XPS measurements on CLSs for many different bimetallic surface alloys are presented together TDS data for CO desorption. This last measurement gives in some way an idea of chemical reactivity of the surface from which CO desorbs, by investigating the bond strength between CO and metal surface. The trend shown in these data is clear: when the formation of bimetallic alloys results in a shift of the surface CL toward higher BEs, the strength of the bond decreases, as does the chemical reactivity. On the other hand, when the surface CL shifts in the opposite direction we have an enhancement of the surface chemical reactivity.
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Figure 8. Oxygen chemisorption on 1 Pd ML @Ru(0001). a) Time-resolved spectra collected during the oxygen exposure; b) clean and 60 L oxygen exposed spectra; c) LEED pattern after oxygen exposure.

This is in agreement with our findings in the oxygen chemisorption experiment, despite the differences between oxygen and CO chemisorptions. The first Pd pseudomorphic overlayer grown on Ru(0001) exhibits a large shift toward higher BE, and also manifests a decreased chemical reactivity in comparison with Pd(111) surface.

The second structure we tested by oxygen exposure at room temperature was the two Pd pseudomorphic overlayers on Ru. We used the same procedure, albeit with a small difference in the timing of the pressure’s steps and with a total oxygen amount of 70 L instead of the 60 L exposure used previously.

In Fig. 9a all the time-resolved mode spectra are shown. In this case the lineshape clearly evolves and in Fig. 9b both clean and 70 L-exposed spectra are shown, to highlight the large modification in CL induced by oxygen exposure.

Figure 6b shows the analysis for the clean 2 Pd MLs: the lower BE component is the surface one, the higher BE peak arises from Pd atom on the interface layer. During oxygen exposure surface component decreases and the interface component apparently seems to grow in intensity. The reason is that a new component arises, generated from Pd surface atoms coordinated with chemisorbed oxygen. The reason for the apparent increase of interface signal is because the BE of this new component is very close to the interface peak. The shift between these two components, determined by multicomponent fit analysis (results shown in Fig. 9c), is about 30 meV, at a BE of 335.29±0.02eV. The surface component,
after the oxygen chemisorption, undergoes to a 510 meV CLS, showing a good agreement with the Pd(111) single crystal behaviour. In that case, after the oxygen exposure, the clean surface component, at a 334.6 eV BE, decreases, whereas a new component, at a 335.2 eV BE arises, with a 600 meV shift. The difference between these two oxygen-induced shifts has the same origin of the 180 meV shift between the Pd(111) singel crystal surface and the surface layer of the 2 Pd ML structure: the strain induced by the Pd growth on the Ru(0001) substrate.

Figure 9. Oxygen chemisorption on 2PdML@Ru(0001). a) time-resolved spectra collected during the oxygen exposure; b) clean and 70L oxygen exposed spectra; c) multicomponent fit analysis for oxygen exposed spectrum: the blue component arises from Pd surface atoms coordinated with oxygen atoms, yellow and grey peaks arise respectively from clean surface and interface Pd atoms.

For the fitting analysis of all collected spectra we used the same lineshape for the three components, with a constraint on the interface peak intensity. Assuming small screening effects or, in the same way, small photoelectron diffraction effects, induced by oxygen chemisorption, the interface intensity has been maintained at a fixed value. In Fig. 10 the three components’ intensities are shown, plotted as a function of the oxygen exposure. The clean surface Pd component (whose intensity has been used as normalization factor for all intensities) decreases from 1 to 0.75 and the Pd oxygen-coordinated component increases from 0 to 0.21. The small difference between the two trends could be explained by photoelectron diffraction or screening arguments, but nevertheless the small discrepancy is in good agreement with the “small effect” hypothesis we used to constrain the interface intensity at a constant value.
Figure 10. Peak intensities vs. oxygen exposure. The fitting was performed with the interface intensity fixed and by imposing the same lineshape for the three components.

In oxygen chemisorption on fcc (111) and hcp (0001) surfaces oxygen atoms go on threefold sites. This means that for every oxygen atom on Pd surface three Pd atoms undergo to a shift in their CL. If the intensity of the clean Pd surface component decreases by 25% this means that the oxygen coverage is 0.25 divided by three, so oxygen coverage in this case is about 0.08 ML. As stated previously, Pd(111) after 20 L of oxygen exposure is saturated with a (2x2) structure with a 0.25 ML coverage. This means that the chemical reactivity of 2 Pd ML is larger than 1 Pd ML one but lower than the reactivity of pure Pd(111). Also in this case we find a perfect agreement between CLS and variation of chemical reactivity: 2 Pd ML structure has a surface CL shifted toward higher BE and a lower chemical reactivity respect to Pd(111), relationship that is inverted in comparison to 1 Pd ML structure.

In conclusion, we have a good experimental evidence of the reliability of CLS measurements as an experimental indicator of chemical reactivity of solid surfaces.
Reference

The technology for depositing small amounts of atoms onto well-prepared surfaces under high vacuum has undergone significant development since its inception 40 years ago, and is now very sophisticated. It is possible to prepare novel structures in two (atomic monolayers), one (atomic chains) and zero (nanoclusters) dimensions, using a variety of materials, and to study their atomic structure and electronic properties [1-3].

One of the fastest-developing fields in surface science over the past several years has been the study of nanoclusters of semiconducting and metallic materials [4-13]. The motivations for these studies come from a diverse set of potential and already realized applications, as well as from fundamental chemical and physical interest. In fact, one particularly appealing aspect of this field is the strong overlap between basic and applied research. Applications include the use of nanocrystals as structural materials, chemical catalysts, critical components in advanced electronic architectures, and more. The fundamental scientific issues are also broad and include the elucidation of size-dependent scaling laws, the chemistry of size and shape, photophysical processes in confined geometries, as well as others.

Metal nanoclusters have been studied in many different ways: as free clusters, as embedded in a host matrix or deposited onto a support. This chapter will deal with the latter.

Supported nanoclusters are interesting for many reasons, the foremost being that real catalysts are usually aggregates of TMs and some metal oxide, so their function is tied to the interaction between the two chemical species. For this reason, a supported nanocluster could be one of the best model systems for understanding the working principles of more complicated systems, like nanopowders. By properly choosing a support with desirable characteristics, as well as its thickness, charging problems that often plague spectroscopic studies of insulating supports can be avoided. For example, when using thin metal oxide films that are sufficiently conductive via defects or tunneling to the metal substrate no significant charging occurs. Other important reasons that usually guide scientists in the choice of the right support are the thermal stability and the chemical interaction with the environment, qualities found in certain carbon based supports.

The subject of this chapter is the characterisation of Pd nanoclusters growth on different carbon-based supports. We performed HRPES measurements for
different amounts of Pd deposited on spaghetti-like Single-Walled Carbon NanoTubes (SW CNTs), on Highly Ordered Pyrolytic Graphite (HOPG) and on a single graphene sheet grown on an Ir(111) surface. These three experiments aim to provide us with a deeper understanding of the Pd atoms’ nucleation mechanisms on carbon-based supports, and to the study of the thermal stability of these nanocompounds, including the manner in which they break up. Another interesting topic is the interaction of the support with the TM, and the influence of the support’s morphology on the formation of clusters. As will be shown, the use of different supports emphasized the importance of metal-support interaction and played a key role in the interpretation of experimental results. Examination of the data from three different experiments with regard to the known differences between supports, provided a deeper understanding of the clusters’ growth mode and their electronic properties.

Before presenting the experiments and their analysis it is important to acknowledge that part of this work has been done in collaboration with Prof. S. de Gironcoli at SISSA and his research team. The analysis of the data has guided the approach of their theoretical calculations and similarly, the theoretical results provided insight to proper interpretation of the experimental data.

4.1 Pd nanoclusters on SWCNTs and HOPG

The sample preparation and measurement was performed on the SuperESCA beamline at the ELETTRA synchrotron radiation laboratory, as described in the previous chapter. A commercial "bucky paper" made of SWCNTs with average diameter of 1.3±0.1 nm and an HOPG substrate were mounted on a sample holder, composed of Ta clips with two circular windows which exposed the deposition zones, as schematically shown in Fig. 4.1a. Both of the samples were resistively heated, and the temperature was determined with an uncertainty of ±30 K from the current passing through the sample, in combination with a pyrometer and a thermocouple welded to the Ta clip. The manipulator was introduced in the UHV chamber immediately subsequent to cleaving the HOPG support. To complete the HOPG preparation several annealing cycles up to 1200 K were performed until a sharp C 1s core level was measured. The CNT sample was prepared with repeated annealing cycles up to 1800 K until no traces of chemical contaminants could be detected by photoemission [14].

The Pd evaporator (Fig. 4.1b) is the same used in the experiment reported on Chapter 3. The metal source was gradually heated and then held at the evaporation temperature for a fixed amount of time. The pressure in the UHV systems was always kept below $4 \times 10^{-10}$ mbar to prevent the adsorption of background impurities.

The overall energy resolution (electron energy analyser and x-ray monochromator) was 40 meV for both Pd 3d$_{5/2}$ and C 1s core level spectra. The electron binding energies are referred to the Fermi energy position, measured under the same experimental conditions (photon energy, analyzer setup, and surface temperature), from a Pd polycrystal mounted on the bottom of the sample holder (see Fig. 4.1b). The data analysis method has been already described in the previous chapter.

The goal of the experiment was to study the clusters’ growth mechanism and structure, as well as to evaluate their thermal stability. We investigated different
amounts of Pd deposited on the two supports at liquid nitrogen (LN) temperature and the evolution of photoemission spectra after annealing to room temperature (RT), 200°C, 400°C, 600°C and 800°C. After every evaporation (15, 60 and 240s of Pd deposition time with a constant Pd filament current, constant filament-support distance and the same turn-on procedure) and after every annealing we performed each of the measurements (Pd 3d$_{5/2}$, C 1s and valence band (VB) spectra). An overview spectrum, comprising Pd 3d$_{5/2}$ and C 1s with the same pass energy, was recorded only directly after Pd deposition, since it was only intended to allow the deposited quantity of Pd to be determined by the intensity ratio of the two components. At the end of every measurement shift the sample was cleaned with a 5 minutes annealing at 1050°C, for removing all traces of Pd.

4.1.1 Pd coverage determination.

One way for evaluating the Pd quantity on different supports is the comparison between Pd 3d$_{5/2}$ and C 1s peak areas in spectra collected with the same photon and pass energies. For this evaluation we used Pd@HOPG spectra, because HOPG is a smooth and well ordered, while the SWCNTs are highly corrugated and disordered, thus the Pd atoms might end up under a CNTs’ skin that would screen the Pd signal.

**Figure 4.2.** C 1s and Pd 3d$_{5/2}$ overview spectra for different Pd deposition times. The three spectra have a vertical offset for distinguishing the different curves on from each other.
In Fig. 4.2 overview spectra are shown, for three different exposure times. For clarity the spectra are offset vertically to eliminate overlap. Before calculating the peaks’ areas a linear background was removed. To determine the Pd coverage the numerical values obtained for the peaks’ areas were weighted with the Pd 3d and C 1s cross sections at the used photon energy. The model for the coverage evaluation is based on simple assumptions of the inelastic mean free path of the photoelectrons from a layered structure. As shown in Fig. 4.3 the outcoming photoelectrons pass through a varying number of layers of different material. For an evaluation of the signal attenuation we must consider the material-specific mean free path for the different kinetic energies and average on the number of atomic layers that photoelectrons can meet.

As suggested by Freund et al. [15] we suppose that cluster height does not exceed 5 atomic layers, so hypothesizing a Poisson distribution of the cluster heights we can approximate the thickness mean value to about 2 atomic layers. Under the hypothesis that the photoelectron signal (at the kinetic energies involved in our experiment) is negligible after a 5-layer path, we can write down the two formulas for the evaluation of the Pd coverage:

$$I_{Pd3d} = \alpha \cdot \exp\left(\frac{n \cdot a_{Pd}}{\lambda_{Pd}(KE)}\right)$$

$$I_{C1s} = (1 - \alpha) \cdot \sum_{n=0}^{4} \exp\left(\frac{n \cdot a_{C}}{\lambda_{C}(KE)}\right) + \alpha \cdot \exp\left(\frac{n \cdot a_{Pd}}{\lambda_{Pd}(KE)}\right) \sum_{n=0}^{2} \exp\left(\frac{n \cdot a_{C}}{\lambda_{C}(KE)}\right)$$

where $I_{C,Pd}$ are the photoemission intensities weighted by cross sections, $\lambda$’s are the IMFPs in different media at different KEs and $a_{C, Pd}$ is the lattice constant in the direction normal to the surface. The only unknown value is the coverage $\alpha$ but a two-equation system is not redundant because we want an expression of $\alpha$ in terms of total area percentage. After calculations we find these values for $\alpha$: 

Figure 4.3. Different normal emission paths for photoelectrons outcoming from a layered structure. The red crosses indicate the occurrence of the inelastic scattering events.
This is a reasonable result, though it is affected by uncertainties introduced by the strong assumptions (the Poisson distribution of clusters’ height, the use of the universal curve for the evaluation of the mean free paths, etc.).

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In addition to the overview spectra comparison we used also another method for the coverage evaluation. Thanks to image processing of SEM data of the Pd nanoclusters on CNTs, we may compare these results with a direct measurement of the Pd covered area. In Fig. 4.4 we find the two images of Pd nanoclusters on CNTs for 15 s and 240 s deposition times. Next to the SEM images clusters’ size distribution is shown. The image processing gives coverage values of 1% and 15% for 15 s and 240 s deposition times (with an average Pd atoms numbers of 200 and 10000 respectively), in rough agreement with coverages found with the peak comparison. Nonetheless, the most important point is that for the maximum coverage we can be sure that the support area occupied by Pd nanoclusters is less than 20%, and therefore low enough for our experiment. At low coverages small sized clusters formation is favoured and so the detection of low coordinated atomic species could arise from our analysis.
4.1.2 First theoretical results: some indications for data analysis

The first study of the Pd-graphite interaction was the calculation of BE between adatoms and the substrate. When isolated atoms are adsorbed on the graphite surface the most stable site is the bridge site, with a BE of 1.12 eV. The Pd-C bond on top sites is slightly weaker, 1.09 eV, whereas the hollow site has a BE of 0.91 eV. When the same calculation is repeated for dimers and trimers, a trend arises: the bond between Pd and the substrate becomes weaker, while the Pd-Pd interaction dominates the full BE. In Fig. 4.5 the Pd-substrate BE per atom is shown, for different configurations of adatoms, dimers and trimers.

![Bar chart showing binding energy between Pd atoms and graphite support](image)

**Fig. 4.5. Binding energy between Pd atoms and graphite support (for one single atom) calculated for different configurations of adatoms (grey), dimers (red) and trimers (green). The abbreviations are indicative of the number of the atoms composing the cluster and the sites that these atoms occupy. For example, HB1 and HB2 are two different configurations of a two-atoms cluster with one atom on a bridge site and one atom on a hollow site; BBB1 and BBB2 are two distinct configurations of a three-atoms cluster with all the atoms positioned on bridge sites, and so on.**

The next characteristic to understand was the height of diffusion barriers for a Pd adatom on a defect free HOPG surface. These calculations have been performed using the Nudge Elastic Band (NEB) method, a tool belonging to the transition state theory. As noted above, bridge sites are the most favourable positions for Pd atoms on a graphite support, so we focused our attention on the bridge-bridge and the bridge-hollow-bridge transitions. The results of these calculations are summarized in Fig. 4.6a.

This is the second important point: Pd adatoms have a very high mobility on defect-free HOPG: diffusion barriers of 0.03 and 0.19 eV allow high mobility even at LN temperature. Similar calculations were also performed for dimer and
trimer surface diffusion, and the results, shown on the right side of Fig. 4.6, clearly show that energy barriers are also very low for small clusters. Further NEB calculations show other interesting features of the Pd-HOPG interaction. For example, the “tunneling” of a Pd atom from one side to another of a graphene sheet is forbidden, since these transitions have an energy barrier of about 12 eV. We have also determined the mechanism for the transition from two dimensional to three dimensional clusters. This simulation was done using a 4 atom ensemble, with one atom that undergoes motion from the graphite support to the top of the 3-atom planar cluster. As depicted in fig. 4.7, the barrier for the 2D-3D transition is significantly lower than the one for the opposite process.

**Fig. 4.5.** a) Energy barriers for bridge-bridge and bridge-hollow-bridge sites hopping for a Pd adatom on a defect free HOPG surface; b) Energy barriers for adatom, dimer and trimer surface diffusion.

**Fig. 4.7.** Activation energies for 2D↔3D transition, calculated for a 4-atom cluster.

The last important calculation deals with the cluster aggregation and segregation mechanisms. This simulation was performed with a 7 atom ensemble, arranged as shown in Fig. 4.8. When the “on top” atom is removed from the cluster and brought far enough away so as not to interact with the other atoms, the energy barrier (3.06 eV) is higher than the same quantity calculated for the removal of a “side” atom (2.11 eV). The calculation for the opposite process (the approach of a Pd atom to the cluster) shows a very low activation energy (0.044 eV).
Fig. 4.8. Cluster aggregation and segregation barriers for an incoming/outgoing side Pd atom. The barrier for the same process with a “on top” atom is more expensive.

Taking all of these first results into account, we can summarize:

- no adatoms or even very small clusters will be found, because of many reasons. Primarily, the very high mobility on the graphite surface obtained by NEB calculations for adatoms and small clusters. Additionally, the energy gain in cluster aggregation favors larger cluster growth.
- Pd does not wet the HOPG surface. The 4-atom NEB calculation shows that a 3D structure is more favourable than the 2D configuration and if a planar configuration is imposed on the 7-atom ensemble, the relaxation of the cluster produces a 6-atom planar configuration with an “on top” atom.
- the cluster segregation is expected to start from cluster sides, in particular from the Pd atoms coordinated with the graphite support. This because the Pd-Pd bond is stronger than the one between Pd and C.

After these preliminary considerations we can begin a first approach to the analysis of the experimental data.

4.1.3 First data analysis: C 1s and Pd 3d5/2

As previously mentioned in the introduction, we measured Pd 3d5/2, C 1s and valence band spectra for every Pd coverage and for each annealing step. C 1s spectra are not particularly useful for understanding cluster structure; as shown in Fig. 4.9, when some amount of Pd is deposited on clean HOPG, the sharp one-component C 1s spectrum is attenuated by Pd screening and is also split into two components, one arising from the bare portions of the surface (yellow peak), and the other from the C atoms coordinated with Pd (blue peak). There is a small shift between these two components (60 meV) and this is in good agreement with preliminary calculations. A small shift implies a weak C-Pd interaction, as revealed by BE calculations for small clusters.

After this cursory overview of the C 1s spectra we focus on the analysis of the Pd 3d5/2 data. In Fig. 4.10 and 4.11 all Pd spectra are shown, for Pd deposition on CNTs and on HOPG supports, respectively. For every Pd coverage, the annealing progression goes from LN temperature deposition (black spectrum) to the highest annealing temperature (light grey spectrum). However, before beginning with the systematic analysis and discussion of the spectra, it is worth noting some qualitative trends to determine the best approach.
Chapter 4 – Pd nanocluster on carbon based support

**Figure 4.9.** $C 1s$ spectra before and after the deposition of 0.15 Pd ML on a clean HOPG surface. The intensity of the yellow peak is strongly reduced after Pd deposition and a new peak arises from C atoms interacting with Pd atoms.

In literature there are many works (both theoretical and experimental) on Pd single crystals, and it is well known that the bulk generates a CL component at a BE of 334.9 eV, whereas the Pd(111) surface component is shifted toward lower BE by about 0.3 eV [16]. In Figs. 4.10 and 4.11 a line indicates the position of bulk Pd $3d_{5/2}$ peak for reference. With few exceptions (such as the low coverage and low temperature spectra) every spectrum seems to have one component at the “bulk” position, and almost every spectrum contains two additional components, one on each side of the bulk line. At first glance there are two main indications:

- low coverages have a larger contribution at high BEs,
- with increasing annealing temperature two effects arise: the growth of the high BE contribution to the spectra, and the shift of the spectrum’s intensity maximum (see the red circles in Fig. 4.10).

Starting with these simple observations we decided to use a three component fitting curve, with the reference peak at a BE around the bulk line and two additional peaks, one on each side.

In fitting these spectra we opted to preserve the lineshape where possible, imposing a tight restriction on the variation of the Lorentzian width and asymmetry parameter, while allowing a wider range for the Gaussian width and peak position. In the successive figures (from 4.11 to 4.13) all the spectra with the multi-component fitting are shown.
Figure 4.10. Measured Pd 3d\textsubscript{5/2} spectra for three different amounts of Pd on carbon nanotubes (a) and HOPG (b) support. The blue line indicates the position of the bulk component [16] as a reference, the red circles highlight the drifting of the intensity maximum of each spectrum in the CNT series. The grey scale indicates the temperature progression, from the LN deposition (black) through RT, 200°C, 400°C, 600°C and 800°C annealings.
Figure 4.1. Pd 3d\textsubscript{5/2} spectra deconvolution for 0.15 Pd ML coverage, deposited at liquid nitrogen temperature, on CNT (a) and HOPG (b) support and subsequent annealing steps.
Figure 4.12 Pd 3d_{5/2} spectra deconvolution for 0.04 Pd ML coverage, deposited at liquid nitrogen temperature, on CNT (a) and HOPG (b) support and subsequent annealing steps.
Figure 4.13. Pd 3d₃/₂ spectra deconvolution for 0.01 Pd ML coverage, deposited at liquid nitrogen temperature, on CNT (a) and HOPG (b) support and subsequent annealing steps. A new component (violet peak) appears, not present in the other spectra.
To summarize these results, in the following three figures (4.14 to 4.16) the trends of Gaussian widths, positions and areas (overall intensity) of each component are plotted as a function of the annealing temperature. As previously stated, we used a three component Doniach-Sunjic lineshape for the fitting Pd spectra, with a central peak, initially positioned at a BE close to the bulk value reported in literature, and two further components, one on either side of the bulk. The main trends determined from this analysis are the following:

- **High Pd coverage**
  - the blue peak is located at 334.95±0.05 eV, very close to the bulk value and the shift of the yellow peak with respect to the blue one is very close to the Pd(111) SCLS (0.3 eV, [16]). This is in good agreement with our estimate of cluster size (about 10000 atoms): at this scale bulk and surface signals could arise and dominate other components.
  - with successive annealings the bulk component loses intensity faster than the other components. This behavior is due to the cluster evaporation: the cluster size decreases and the surface/bulk intensity ratio increases.
  - there are no significant differences between the HOPG and CNT spectra, because of the relatively low weight of the cluster portion that interacts with the support with respect to the overall cluster signal.

- **Intermediate Pd coverage**
  - the SCLS is still observed but the behaviour of bulk and surface components is not understood as simply. At low temperatures (LN and RT) the bulk/surface ratio is higher than for larger clusters (the opposite of the expected trend), and above 200°C the surface component becomes more intense than the bulk component. Meanwhile, the grey component’s weight is the main difference with respect to the previous coverage.
  - some appreciable differences begin to arise between CNTs and HOPG spectra. The grey component is the principal one in the CNT spectra, whereas the HOPG spectra are still dominated by bulk and surface components. Furthermore, the peaks’ Gaussian widths for CNT are slightly larger than for HOPG.

- **Low Pd coverage**
  - CNT and HOPG spectra are now completely different. In HOPG spectra we find only two peaks (the surface peak has vanished), with the grey peak dominating over the blue. In CNT spectra both the surface and also the bulk components have vanished. In their place, a new component (violet peak in fig 4.13a) is observed, with a BE 500 meV higher than the grey one.

After this overview of experimental data, a comparison with theoretical calculations of CLSs is required, in order to understand the chemical environment of the atoms giving rise to each component. Indeed, “bulk” and “surface” are names given for simplicity and a more realistic and precise interpretation must be achieved.
Figure 4.14. Trends for Gaussian width, BE and area of spectra component for the 0.15 ML coverage.
Figure 4.15. Trends for Gaussian width, BE and area of spectra component for the 0.04 ML coverage.
Figure 4.16 Trends for Gaussian width, BE and area of spectra component for the 0.01 ML coverage.
4.1.4 Theoretical calculations on CLSs.

CLSs of Pd atoms with various coordinations were calculated, using the same small clusters (4, 7 and 11 atoms) used for the calculations described in section 4.1.2 (adatom-support BEs, 2D-3D transitions). A reference level is needed to obtain absolute values of CL BEs from these calculations, so a double-step operation was performed. For each of the studied configurations an isolated adatom was added far away from the cluster: in this way every calculation had a common energy level. After this step, we calculated the shift of the $3d_{5/2}$ level for each atom of the three clusters, with respect to the that of the isolated adatom. To obtain absolute values of the BE for these shifts, a second step was needed: the collocation of the isolated adatom CL. A new simulation was performed, with a seven-layer Pd slab, with two graphene sheets deposited on the Pd surface and an isolated adatom on the graphene surface, as depicted on Fig. 4.17.

![Figure 4.17](image)

**Figure 4.17.** The system used for the calculation of the shift between CLs of an isolated Pd atom (red), adsorbed on a graphene sheet, and a bulk Pd atom (green). In this way we assigned an absolute value to the CL BE of the isolated atom, used in the following as the reference for all the other calculated shifts.

The Pd bulk CL (the green atoms in the figure) is a well known, determined both theoretically and experimentally, so by this double-reference method every single atom belonging to the three clusters has a CL that can be determined absolutely.
The results provided by these first calculations presented a problem when compared with experimental data: CLs calculated for the nine different atoms belonging to the three clusters have a lower BE than the bulk value. This means that no CL lies in the “grey peak” zone (see Sec. 4.1.3). This result is not completely unexpected: dealing with a more-than-half filled d-band metal low coordination (as the surface has respect to the bulk) usually gives rise to a shift to lower BE of the CLs, and the clusters’ atoms have a coordination from 3 to 9. The interpretation of the high BE, still elusive after this first part of the work, was achieved thanks to a subtlety in the experimental data.

Focusing our attention only on 0.04 and 0.01 ML Pd coverages, we notice several key differences between CNT and HOPG spectra. In Fig. 4.22 a comparison between Pd spectra of the same coverage (0.04 ML) on the two different supports are shown.

**Figure 4.18.** A comparison between HOPG (grey) and CNT (red) spectra for 0.04 ML Pd coverage. The centers of mass of differently supported clusters spectra show a trend: the CNT centers are always shifted toward higher BE.

For every pair of spectra the CNT are always shifted toward higher BE, so we may argue that the origin of the high BE component must be the interaction with the support. Being that the main difference between the two supports is the presence of surface defects (we used SW-CNTs spaghetti like), the hypothesis we tested is that the high BE component arises from Pd atoms bound to surface defects.

The calculations were altered from Pd clusters on a defect free graphene sheet to Pd atoms that nucleate on defective sites of the support. For simplicity two kind of defects have been studied: steps and vacancies. In fig. 4.19 some simulated structure is shown.
Figure 4.19. a) 7-atom cluster on a defect free HOPG surface. b) 4-atom cluster nucleated from a carbon vacancy on the HOPG surface. c) 4-atom cluster nucleated on a step of the HOPG surface. In each of these simulations the isolated atom (red) gives the energy reference for the CLSs.

The red atom is the isolated adatom used as the reference. In the three boxes there are: a seven atom cluster on a defect free graphene sheet, a four atom cluster nucleated on a carbon vacancy and a four atom clusters nucleated on a step. In this second calculation, more than forty inequivalent atoms were studied. As suggested by the difference between CNT and HOPG spectra, defective sites on the carbon support play a key role in the formation of the high BE component.

In Fig. 4.20 the calculated CLs of Pd atoms in many different local configurations, and belonging to clusters nucleating in different sites are shown. These appear in a Pd $3d_{5/2}$ spectrum of 0.04 ML coverage (after 400°C annealing), with the different components arising from fit analysis.

Previous interpretations of the high BE component included the effects of cluster charging during the photoemission process [17] or the effect of charge transfer from Pd to the graphitic layer [18]. Our results strongly support the latter interpretation. We performed theoretical calculations on Pd $3d_{5/2}$ CLs, finding a trend for the effective coordination (a weighted sum of the different bond lengths inside the van der Waals radius), as a function of the BEs.
In the upper panel all the Pd 3d\(_{5/2}\) CL calculated for several palladium atoms among all the simulations are shown. Three groups can be identified: one at low binding energies, where palladium is not coordinated with defect, one at higher binding energies where palladium is highly coordinated with defects and a middle one, where these coordination balance each other. These groups perfectly match with the experimental analysis, reported in the lower panel.

This correlation is shown in the upper panel of the picture. Even if every CLS comes from several contributions, the trend is clear; the low BE region shows a higher effective coordination with Pd atoms, whereas the effective coordination with defective sites is zero. The opposite behaviour is observed for the high BE region: the Pd coordination drops drastically and the defective sites’ coordination clearly grows. The effective coordination with defect-free graphite is not as indicative as the other two quantities and has a relevant value for all the atomic species we studied.
In conclusion, we make few brief remarks on cluster nucleation. Metallic atoms aggregate very easily, due to the high diffusion on the substrate and the most stable nucleation sites are defects. With increasing temperature the clusters break, loosing palladium atoms mainly from the sides, on the edges connected to graphite. At higher temperatures and for lower coverages, clusters will be smaller, containing a high percentage of palladium atoms bound to defective sites. This explains the presence of the high binding energy portion of the spectra and explains the difference between small and large clusters: in large clusters palladium atoms bound to defects are present, but their relative contribution to the spectra is almost negligible. As the cluster dimensions are reduced this component becomes increasingly important, while the bulk component is decreased to vanishingly small intensity.

4.2 Pd nanoclusters on graphene/Ir(111)

The interest in graphene is due to its physical properties, like the extremely high electrical conductivity induced by the unique band structure. In recent years an increasing attention has been focused on the formation of a single carbon layer on metal surfaces, not by carbon segregation from the bulk, as it happened in the past, but with an epitaxial growth based on the dissociation of an hydrocarbons adsorbed on the surface. This new technique allows an excellent control on the result quality and guarantees the formation of a single layer of carbon atoms, with a long range order that remains almost unaffected by the metal surface defects like steps.

![Figure 4.21. The three distinct regions in a Moirè cell, defined by the relative positions of C atoms with respect to Ir substrate atoms.][19]

The graphene/Ir(111) has further features that make it a so interesting system. There is a mismatch between the lattice constants of the graphene and the Ir
surface, that induces a periodic corrugation on the graphene sheet. This periodicity is named Moirè and is due to the local variation of the carbon atoms positions respect to the Ir surface. The periodic structure of this alteration of the smooth surface allows the growth of regular clusters’ matrices. This is possible because in every Moirè cell there exist several zones with different nucleation capability so a well defined topology of cluster formation can be achieved. In Fig. 4.21 the three different zones of a Moirè supercell are depicted. This distinction is based on the different positions of carbon atoms with respect to Ir atoms of the first and second layers (with respect to only first layer atoms there is no difference between fcc and hcp regions). From [20] it is known that nucleation of Ir clusters is favoured in hcp zones and under 160 K starts also in fcc, whereas no cluster formation has been observed in atop zones.

The capability to host regular, well ordered nanoclusters array is not the only difference between the graphene/Ir(111) and the two carbon based support of the previous section. Dealing with HOPG and SWCNTs the only interaction on which focus the attention was the one between the deposited Pd atoms and the surface support. In this case instead we cannot consider the graphene sheet as it was free standing: the presence of the Ir cannot be ignored. In [21] theoretical calculations reveal the existence of an interaction between the Ir substrate and the deposited metal atoms, that generates the pinning of the graphene sheet, as depicted in Fig. 4.22.

Figure 4.22. Side view of a graphene/Ir(111) system modified by the presence of a four atoms Ir cluster, from ab initio calculations [21].

Every sample preparation and measurement was performed on the SuperESCA beamline at the Elettra synchrotron radiation laboratory, as described in the previous chapter. The samples were heated resistively, and the temperature was determined with an uncertainty of ±30 K with a thermocouple welded on the backside. The Ir(111) sample was prepared with cycles of Ar⁺ sputtering and annealing, until no trace of chemical contaminants or metal catalysts could be detected by photoemission. After the Ir surface preparation is accomplished the graphene sheet is formed by several cycles of 100 s long C₂H₄ exposure at 10⁻⁷ mbar pressure and 570 K temperature, followed by the annealing of the system at 1420 K, by which the adsorbed ethylene decomposes.

The Pd evaporator and the deposition procedure is the same already described in the previous chapter, as the experimental setup, the energy resolution and the fitting procedure do.

The aim of this experiment is the characterization of the Pd cluster formation on this support. The role of the support and the temperature effect on the nucleation
mechanism will be evaluated by the survey of Pd 3d\textsubscript{5/2} core level. We investigated different amounts of Pd deposited on the support at -170°C and the evolution of photoemission spectra after annealings to -70°C, room temperature (RT) and 400°C. After every evaporation (30, 60, 120, 300 and 720 s of Pd deposition time with constant Pd filament current, constant filament-support distance and the same turn-on procedure) and after every annealing we performed Pd 3d\textsubscript{5/2} and valence band (VB) measurement, whereas the C 1s and the Ir 4f\textsubscript{7/2} spectra were recorded only directly after Pd deposition.

4.2.1 Preliminary considerations and coverage determination

Before analyzing the Pd 3d\textsubscript{5/2} spectra, as I did in the previous experiment, the Pd coverage of the substrate must be calculated. In this case I compared the results obtained from the overview spectrum, where C 1s and Pd 3d\textsubscript{5/2} core level are measured using the same experimental conditions, with the results obtained from the observation of the changes that occur on Ir 4f\textsubscript{7/2} spectra.

![Ir 4f\textsubscript{7/2} spectra for: (a) clean graphene surface; (b) 0.25 Pd ML deposition. The interaction between the Ir surface layer and Pd deposited atoms generates the fall of the surface component and the rise of a new peak.](image)

**Figure 4.22.** Ir 4f\textsubscript{7/2} spectra for: (a) clean graphene surface; (b) 0.25 Pd ML deposition. The interaction between the Ir surface layer and Pd deposited atoms generates the fall of the surface component and the rise of a new peak.

As stated by Feibelman *et al.* there is an interaction between the deposited atoms and the Ir surface. In Fig. 4.22 the Ir 4f\textsubscript{7/2} spectra for the system before and after the Pd deposition are shown. The Pd presence induces the rise of a new component, at a BE comprised between the bulk and surface signals.

![Pd 3d\textsubscript{5/2} spectra areas for different deposition times. The linear trend is lightly altered only on the last part of the graph, maybe because of the arising of a highest dimensionality of the clusters and the consequent screening effect.](image)

**Figure 4.23.** Pd 3d\textsubscript{5/2} spectra areas for different deposition times. The linear trend is lightly altered only on the last part of the graph, maybe because of the arising of a highest dimensionality of the clusters and the consequent screening effect.
The evaluation of the coverage has been done using data coming from the largest Pd amount: in this way the signal originated by Ir atoms interacting with Pd clusters is more detectable. The other coverages has been calculated supposing a linear trend in Pd deposition by our evaporator. This hypothesis has been confirmed by the calculation of Pd spectra areas: as shown in Fig. 4.23 the peak areas grow linearly as the deposition time increases.

There is a good agreement between the results obtained with the two different methods and the coverages used in this experiment range from 0.01 to 0.25 ML. Also in this case we deal with small coverages, almost the same studied in the previous section so we can expect that something similar occurs in temperature and Pd amount dependence.

4.2.2 Experimental results

In Fig. 4.24 and 4.25 the Pd 3$d_{5/2}$ spectra for respectively low (0.01 and 0.02 ML) and high (0.1 and 0.25 ML) Pd coverages are shown.

![Figure 4.24. Pd 3$d_{5/2}$ spectra for 0.01 and 0.02 ML coverages after deposition and several annealings steps.](image-url)
Figure 4.25. Pd 3d$_{5/2}$ spectra for 0.1 and 0.25 ML coverages after deposition and several annealing steps.

From the bottom to the top the progression in temperature raises, from the deposition at -170°C until the last annealing at 400°C.

In low coverages spectra only two components arise from the fit analysis, whereas in high coverages three components are needed for a good fit procedure with low structureless residual. This situation is similar to the one encountered dealing with Pd nanocluster supported on HOPG and CNTs: also in that case for low coverages only two components arose, with those at high BE that were originated by Pd atoms interacting with surface defects. Here the situation is quite different. In this case high BE components are not due to substrate defects but arise from strong interactions between Pd small clusters and the Ir surface. It is obvious that the small size of the clusters enhances the components arising from the interaction with the support: with a few Pd atoms there cannot be many bonds among Pd atoms and the weight of Pd-substrate interactions in effective coordination increases.

We can also hypothesize that these small clusters had a 2D structure: a 3D structure usually implies three component spectra with the presence of some signal aligned
with bulk and surface (usually <111> oriented) monocrystal signals. Some trace of three dimensional and more ordered structure arise only after the 400°C annealing: in those spectra blue and yellow components start to arise, even if with very low intensities.

The situation is quite different in high coverages spectra. The blue and yellow peaks, positioned at the same BEs of Pd(111) bulk and surface signals respectively, are present since the deposition at low temperature, even if the intensity of the surface component becomes remarkable only after the 400°C annealing. The trend of yellow peak has not a so simple interpretation. Its decrease after the first two annealing and its raise after the last one should mean that this signal arises from different atomic species and this hypothesis is supported by the peak broadness. Probably only after the last annealing a well ordered (111) surface is formed and in the low temperature spectra the signal arises from undercoordinated Pd atoms without in a disordered arrangement. The grey peak, shifted by about 300 meV with respect to the bulk line, is present in each spectrum and its contribution is larger in 0.1 ML than in 0.25 ML series, as expected by the considerations on the coordination with the support as a function of the coverage. The violet component, shifted by about 1 eV with respect to the bulk line, vanishes at high coverages so we can argue that it was generated by Pd atoms with the lower coordination with other Pd’s and for this reason with a stronger interaction with the Ir surface. Being the grey component so strong also at high coverage and after every annealing we can suppose that even if clusters have now a 3D structure the aspect ratio height/width must be low, because of the low screening effect on the Pd interface layer.

In conclusion, the role played by surface defects in CNTs (and, in a minor way, in HOPG) here is played by the Ir substrate. Even if Pd atoms are forbidden to undergo to the graphene sheet (the breakthrough of the carbon layer has a very high cost, of about 10 eV) the charge exchange is strong and generates a well detectable CLS of Pd $3d_{5/2}$ towards BEs higher than the Pd bulk signal. A comparison between the high BE components shifts on CNTs/HOPG and graphene supports reveal that similar values occur, even if the origin of these shift is completely different.
Reference

Over the last ten years significant experimental and theoretical efforts have been devoted to the initial stages of oxidation of TM surfaces, motivated by technological applications such as insulating thin films in microelectronics, anticorrosion coatings, and catalysis. After the formation of a chemisorbed oxygen layer, the onset of sub-surface penetration often takes place above a critical coverage, such as has been reported for Ag(111) [1]. For other systems, oxygen exposure at high pressure results in the formation of surface oxides with totally different structures than their bulk counterparts [2] and is accompanied by a significant increase in chemical reactivity [3].

The interaction of a system with oxygen, and thus the oxidation process, may also be indicative of the system’s chemical reactivity. In chapter 3, for example, the interaction of pseudomorphic Pd overlayers deposited on a Ru(0001) surface in a low pressure of oxygen was investigated and a clear correlation between oxygen adsorption and CLS was found.

During recent years a great number of studies have focused on the interaction between oxygen and various Pd-based structures, from single crystals with low-index order or stepped surfaces, to oxide-supported nanoparticles. Understanding and controlling chemical reactions involving nanoparticles are important milestones for future nanotechnologies and, in the Pd case, for the enhanced performance of catalysts which could be used in many applications, ranging from fuel cells and chemical production to electronic sensors for automotive or environmental monitoring. A key problem which has not yet completely addressed is the oxidation of Pd nanoparticles under industrially and environmentally relevant conditions, which should be described on a microscopic level.

It has long been known [4] that if the clean Pd(111) surface is exposed at room temperature to 20 L of O$_2$ even at low pressure (1·10$^{-8}$ mbar), the O-(2×2) structure with an oxygen coverage of 0.25 ML is formed. If the exposure is doubled the surface is unchanged, but if the sample is heated to 250°C or higher, subsurface oxygen penetration takes place [5]. Increasing the pressure (5·10$^{-6}$ mbar) and the total oxygen dose (3000 L), with a sample temperature of 300°C, an incommensurate surface oxide is observed, possessing a two dimensional structure which bears no resemblance to bulk oxides [6]. An exhaustive work on Pd(111) oxidation within a wide range of pressures (from 10$^{-6}$ to 1 Torr) and
temperatures (from room temperature up to 600°C) is found in [7]. The main result is a phase diagram in which conditions for the surface, subsurface and bulk oxides are shown. Similar results are shown in [8], along with the discovery of one more oxygen phase: the supersaturated O_{ads} layer, which coexists with the 2D surface oxide up to 150°C. In this work it is also shown that 2D surface oxide phase saturates between 330 and 380°C and vanishes around 450°C.

In Fig. 5.1 we present a brief summary of the main XPS results for the oxidation of Pd(111). Pd 3d_{5/2} sequence starts with the clean sample, showing the bulk and (111) surface components with the well known -0.3 eV SCLS, going on with the spectrum arising from the oxygen chemisorption with a p(2x2) structure. From this chemisorbed phase a new peak arises, with a +0.3 eV shift with respect to the bulk component. With increasing the oxygen exposure new structures are formed: the II and III peaks, coming from Pd atoms bounded to respectively two and four oxygen atoms, characterize both the surface and subsurface oxide. The II and III are shifted by 0.6 and 1.2 eV with respect to the bulk line. The bulk oxide atoms results instead in a single component, at 1.5 eV from the same reference.

Figure 5.1. Deconvoluted Pd 3d_{5/2} (left) and O 1s - Pd 3p_{3/2} (right) CLs of a) clean Pd(111), b) chemisorbed O-(2x2)/Pd(111), c) surface oxide (Pd_{3}O_{4}), d) subsurface oxide, e) bulk PdO [8].
In O 1s series the single peak arising from the chemisorbed oxygen splits in two components, induced by oxygen atoms bounded to three and four Pd atoms that compose the 2D surface oxide. Nothing changes with the formation of subsurface oxide, whereas the bulk oxide induces in O 1s spectrum two new components: one arises from oxygen atoms in bulk oxide, the other is probably induced by the oxygen in terminal layer.

The Pd nanoclusters oxidation was been also studied, with a special attention on metal-oxide supported nanoparticles. In [9,10] quantitative studies of the interaction between oxygen and an a Fe₃O₄-supported Pd model catalyst by molecular beam (MB) methods, time resolved IR reflection absorption spectroscopy (TR-IRAS) and photoelectron spectroscopy (PES) using synchrotron radiation are found. The oxide is formed with a lower exposure than with single-crystal Pd: oxygen predominantly chemisorbs on metallic Pd for temperatures up to 180°C, whereas at 230°C and above (10⁻⁶ mbar effective oxygen pressure, 130 L of exposure) large amounts of Pd oxide are formed. These Pd oxide species are formed preferentially in a thin layer at the particle/support interface, stabilized by the iron-oxide support. Analysis of the photoemission data does not show a clear spectral multicomponent decomposition as found for HRPES measurements in [8].

In [11] the oxidation behavior of Pd nanoparticles grown epitaxially on MgO(100) single crystal substrates was investigated. The interaction of oxygen with octahedral Pd nanoparticles at 230°C leads to modification of the cluster’s size and shape, with a strong dependence on the oxygen pressure. There is no evidence for the formation of any of the previously reported Pd surface oxides on the (100) and (111) particle facets. A novel nanoparticle oxidation mechanism is found: the Pd particles act as dissociation centers for O₂ and simultaneously serve as sources of Pd atoms, resulting in epitaxial PdO growth on MgO(100).

In [12] the interactions of O₂ with Pd nanoparticle on Al₂O₃(0001) has been studied for both high and low oxygen pressure. After 30 L exposure at 330°C no oxide formation takes place but during the heating the O_ads penetrates in the subsurface region or maybe in the interface region, starting to desorb only over 500°C. For high O₂ exposure an almost complete particles’ oxidation is obtained and the oxide (interpreted as bulk oxide or, for larger cluster, as an oxide shell surrounding a Pd core) has a thermal stability higher with respect to the Pd oxide formed on a single crystal, as observed in [10].

In a large number of investigations on the chemical reactivity of carbon-supported Pd nanoclusters no research has been done on the particles’ oxidation. In this chapter we report on our study on temperature effects and oxygen exposure to understand oxidation mechanism of Pd nanoclusters grown on SW-CNTs, as well as the thermal stability of the obtained oxide structures.

5.1 Experimental

All sample preparations and measurements were performed on the SuperESCA beamline at the Elettra synchrotron radiation facility, as described in the previous chapters.

The sample mounting and the Pd evaporator are those already described in chapter 4 (see Fig. 4.1). The CNT sample was prepared with repeated annealing cycles up to 1800 K until no trace of chemical contaminants or metal catalysts could be detected by photoemission. The metal source was gradually heated and then held
at the evaporation temperature for a fixed amount of time. The pressure in the UHV systems was always kept below $4 \times 10^{-10}$ mbar to prevent the adsorption of background impurities. We limited our investigation to a constant Pd amount, using the same evaporation parameters as the 0.15 ML deposition of Chapter 4. The Pd $3d_{5/2}$ spectra confirmed the same three-component structure with the same CL lineshape and the overview spectra showed the same C $1s$ / Pd $3d_{5/2}$ ratio found previously. These results confirm the reproducibility of the amount of Pd deposited and the clusters’ size.

We performed several oxidations, using three different sample temperatures (150°C, 300°C, 400°C) and three different oxygen doses (70 L, 3 kL and 600 kL). After each oxidation we collected Pd $3d_{5/2}$, O $1s$ and C $1s$ spectra, then we started with an annealing cycle, at temperatures relevant for the oxidation process, recording Pd $3d_{5/2}$ and O $1s$ spectra, to evaluate the thermal stability of the oxide features. The considerations on energy resolution, sample mounting and fit procedure are the same of the previous chapter.

The experiment can be divided in three parts:

- temperature effects (150, 300 and 400°C) during oxidation at low oxygen exposure (70 L)
- temperature effects (150, 300 and 400°C) during oxidation at high oxygen exposure (600 kL)
- oxygen exposure effects (70 L, 3 kL and 600 kL) during oxidation at 300°C

For each of these sections we show the analysis of the Pd $3d_{5/2}$ and O $1s$ spectra, with some brief consideration on C $1s$ spectra for the large exposure. The multicomponent fit analysis is affected by the same problems already found in the previous chapter: the peaks’ position can change by several hundreds of meV and CL lines are very broad, reflecting the large variety of atomic species from which these peaks arise. These difficulties are more evident as the single component intensities become weaker. For these reason the fit analysis was conducted only on the spectra recorded just after the oxidation, where the peaks arising from the interaction between Pd and oxygen are strongest.

5.1.1 Low oxygen exposure

The first experiment we consider is the oxidation of the Pd nanoparticles with 70 L dose of molecular oxygen, at temperatures of 150, 300 and 400°C. In Fig. 5.2, 5.4 the three data series for Pd $3d_{5/2}$ and O $1s$ are presented. Every spectra sequence is composed by the clean sample measurement (black), the after-oxidation measurement (thickest line) and the complete series of spectra collected after each annealing step. The annealing temperatures are different in the three cases and arrive until a maximum of 600°C-800°C.

The first thing we observe from the rough data is the good thermal stability of the species generated by the oxidation with respect to the resistance shown by oxide phases formed on single crystal in [6-8], but it’s not an obvious argument. In the Pd spectra we can see that in the 150°C and 300°C series, moving from the black trace (clean Pd) to the thickest trace (the spectrum measured just after the oxidation) some peak clearly grows at higher BE.
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Figure 5.2. Pd 3d\textsubscript{5/2} spectra for 70 L O\textsubscript{2} exposure at three sample temperatures. The thickest coloured spectra in each series are collected at the bottom of the figure, the black traces correspond to the clean Pd. The other spectra of the series were recorded after each annealing step.

However, after the first annealing the spectra are shifted back towards lower BE, losing a large portion of the higher BE component. In the 150°C series the spectra return to the “clean” shape after annealing to 350°C, in the 300°C series this occurs after annealing to 400°C. In the 400°C series all the spectra have the same lineshape and do not seem to have any additional components after the oxidation. These considerations seems to indicate that the thermal stability limit of the species that originate from Pd-O interaction with an oxygen dose of 70 L is around 400°C.

Figure 5.3. O 1s spectra (superimposed on the Pd 3p\textsubscript{3/2} line at a 531.7 eV BE) for 70 L of O\textsubscript{2} exposure for the three sample temperatures. The black traces correspond to Pd 3p\textsubscript{3/2} from clean clusters. The thickest coloured spectra of each series are collected at the bottom of the picture. The other spectra of the series were recorded after each annealing step.

On the other hand, the observation of O 1s spectra, shown in Fig. 5.3, leads to different conclusions: here the thermal stability limit appears higher, maybe because the O 1s spectral lineshape is more sensitive to the presence of the oxide environment than Pd spectra. The 150°C series returns to the black line shape (the
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Pd $3p_{3/2}$ CL of clean clusters) around 400°C and the 300°C and 400°C series show a higher resistance to thermal treatment, returning to the “clean Pd” shape after annealing to 600°C. This confirms the findings of [10,12], where higher thermal stability for nanoclusters oxide species have been revealed for Fe$_3$O$_4$ and Al$_2$O$_3$ supports.

After this first look at the rough spectra and these considerations on the thermal stability of the “oxide-species” it is worth a deeper investigation by a multicomponent fit analysis.

For the Pd $3d_{5/2}$ spectra we use the lineshape determined from the analysis in the previous chapter, allowing freedom only in the Gaussian width and trying to maintain the “bulk” and “surface” component positions almost constant. We ignored the “defect component” for two reasons. First of all, as previously reported, we choose the highest Pd coverage. This leads to large clusters, in which the defect component has a low weight in the Pd spectrum. Moreover the oxygen-induced components lie very close to the defect component and being all these peaks quite broad, the superposition of too many contributions would be lead to a misinterpretation of the results.

In Fig 5.4 the decomposition of Pd spectra recorded just after the oxidation is shown, with the peak areas’ and BEs’ trends. The violet peaks arise from the Pd atoms unaffected by the presence of oxygen and are centered on the bulk and surface component positions, at 334.9 and 334.6 eV respectively, as clearly appears in the BE trends plot. The blue and yellow peaks arise from Pd atoms coordinated with oxygen. As the area trends show, their intensities drop drastically when moving from oxidation at 300°C to oxidation at 400°C and these two peaks are shifted by 0.4 and 0.8 eV, respectively, with respect to the Pd bulk signal.

There is a well known rule of thumb that point out a linear relation between coordination with an adsorbate and CLS of a surface atom. In [6] the calculations predict the formation of the Pd$_3$O$_4$ 2D structure, with two and four oxygen-coordinated Pd atoms, and the XPS measurements show the presence of two peaks with a shift of 0.6 and 1.2 eV from the bulk signal, so the linear relation holds. Even if our oxide components show different shifts (0.4 and 0.8) there is some suggestions that the origin could be the same surface oxide. The shifts are also in this case one two times the other and between 150 and 300°C the proportion between the two peaks’ areas is about 4, as indicated by the stoichiometry of the structure. Our system shows also a similar behaviour in thermal stability: in [8] the 2D surface oxide is found to vanish at about 450°C, in our measurements the oxidation at 400°C generates very small oxide components if compared to lower temperature oxidations and, as already said, the annealing at 400-500°C changes the Pd spectrum back to the clean cluster lineshape.

Assuming as good this interpretation of XPS data, we can explain the difference in CLSs of oxide phase Pd atoms in many ways. One argument could be the peak broadness. Probably in our spectra we have many distinct unresolved components, because of the presence of differently coordinated surface atoms: what we state as a two components oxide phase could be a many-components phase, in which the 2D surface oxide coexists with low coordinated Pd atoms bound with oxygen in a different environment. Moreover, other unresolved components could arise from the presence of oxygen at the interface between cluster and the support, as stated in [10-12].
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**Figure 5.4.** Multicomponent fit analysis of the Pd 3d$_{5/2}$ spectra recorded after oxidation of the clusters. The violet peaks arise from the clean parts of the clusters. The trend for peak areas and BEs as a function of oxidation temperature are shown. The points at 0°C in the trends’ plots correspond to the values for the clean clusters.

In Fig. 5.5 the decompositions of the O 1s spectra are shown, together with the plot of BE and peak area trends. The violet peak comes from the Pd 3p$_{3/2}$ CL. The fitting was done assuming that this peak contains only one component, due to its broadness, leaving a large freedom in its Gaussian width and position. Assuming the presence of the 2D surface oxide, the blue and yellow components most probably arise from the two oxygen species in Pd$_5$O$_4$ structure, bound with three and four Pd atoms respectively.
Figure 5.5. Multicomponent fit analysis of the O 1s spectra recorded after oxidation of the clusters. The violet peak is the Pd 3p_{3/2} CL. The trend for peak areas and BEs as a function of oxidation temperature are shown.

The O 1s spectra analysis strongly supports the previous interpretation of Pd 3d_{5/2} spectra, because of the BEs of yellow and blue peaks: their relative shift is the same found for the two oxygen species which comprise the 2D surface oxide. The absolute positions of our oxide induced components are rigidly shifted by about 250 meV with respect to the values reported in [6], probably for the same reason of the Pd components shift: the presence of unresolved contribution to CL spectra arising from the undercoordinated surface atoms. Nonetheless, the coupling between yellow and blue peaks, clearly appearing from the their areas’ trends,
support the 2D surface oxide interpretation. The grey component lies in the region indicated in [8] as the supersaturated O$_{ads}$ layer. In the single crystal oxidation, this component comes from oxygen chemisorption over the 0.25 ML saturation studied in [4], rising until a 0.5 ML coverage, and coexists with the surface oxide phase until about 300°C.

The assignment of this component is not so trivial, because even if its BE suggest that it can be due to this denser, chemisorbed phase, its thermal behaviour is the opposite of what found in [8]. In single crystal the supersaturated is the step before the oxide formation and over about 250-300°C it vanishes, as the oxide components increase. In our spectra at 150°C the grey peak is not needed to obtain a structureless residual, whereas for 300°C and 400°C oxidation the fit is not satisfactory without this additional contribution. Maybe the presence of this supersaturated phase needs a surface reordering that, for low oxygen pressure, can be induced only by heating the system.

In conclusion, the most appealing feature found in this first part of the experiment is the formation of an oxide phase even when using a relatively low oxygen exposure, whereas all the Pd single crystal’s oxidation studies show that oxide formation needs much larger oxygen pressure/exposure. This difference could be induced by many factors. First of all, the presence of defects and low coordinated atoms on cluster surface could induce higher reactivity in our nanoclusters. Kinks, steps and edges have here a relevant weight, being the clusters’ average size of about 10000 atoms. Another size induced effect could be also the lowering of energetic barriers for atomic rearrangement, by which the oxide formation, which is most probably accompanied by large restructuring, could be easier.

It is important to mention that even the presence of a different substrate can play an important role: maybe the interface between Pd and CNTs could be a good channel for the oxidation formation, as for the for Fe$_3$O$_4$ support [9,10].

5.1.2 High oxygen exposure

The second part of the experiment, conducted in the same manner, was performed by dosing 600 KL of O$_2$. The highest pressure registered in the chamber was 10$^{-4}$ mbar, but a special gas release system increases the oxygen pressure at the sample surface by a factor of 10, similar to the oxygen pressures used in the experiment described in [8]. In Fig.s 5.6, 5.7 raw spectra of Pd 3$d_{5/2}$ and O 1$s$ are shown.

Regarding thermal stability, there are not large differences respect to the low exposure experiment. In the 150°C and 300°C data series the Pd spectrum returns from the “post-oxidation” to the “clean” lineshape after heating at 350°C and 500°C respectively, a behavior similar to the low exposure case. The 400°C series shows some differences with respect to the other experiments, even though it exhibits a similar general trend. The main difference we observe in rough spectra is the presence of a strong component at about 336 eV BE, readily apparent in the 300°C series. This component vanishes after the first annealing (at 400°C for the 300°C exposure) so its thermal stability seems a bit lower than that of the other oxygen-induced features.
Figure 5.6. Pd 3d$_{5/2}$ spectra for 600 kL O$_2$ exposure at three sample temperatures. The thickest coloured spectra in each series are collected at the bottom of the figure, the black traces correspond to the clean Pd. The other spectra of the series were recorded after each annealing step.

Figure 5.7. O 1s spectra (superimposed on the Pd 3p$_{3/2}$ line at 531.7 eV BE) for 600 kL of O$_2$ exposure at the three sample temperatures. The black curves correspond to Pd 3p$_{3/2}$ from clean clusters. The coloured thickest spectra from each series are collected at the bottom of the figure. The other spectra in the series were recorded after each annealing step.

Looking now only at the spectra measured just after oxidation, we see a large difference in the lineshapes when compared to the previous experiment. In the 150°C oxidation spectrum, where in the low dose case there was a valley (at about 530.5 eV BE), there is a pronounced peak that dominates. In the 300°C oxidation a low BE component arises, which is not evident in the 70 L experiment. In the
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400°C spectrum the strongest feature is a high BE component. All these features represent the most obvious differences with respect to the low-dose data. Subsequent to this first look at the rough spectra, the considerations on the thermal stability of the “oxide-species” and on the main changes induced by the oxygen dose, a deeper investigation by a multicomponent fit analysis is necessary.

![Multicomponent fit analysis of the Pd 3d_{5/2} spectra recorded after oxidation of the clusters. The violet peaks arise from the clean parts of the clusters. The trends for peak areas and BEs as a function of oxidation temperature are shown. The points at 0°C in the trend plots are the values for the clean clusters.](image)

**Figure 5.8.** Multicomponent fit analysis of the Pd 3d_{5/2} spectra recorded after oxidation of the clusters. The violet peaks arise from the clean parts of the clusters. The trends for peak areas and BEs as a function of oxidation temperature are shown. The points at 0°C in the trend plots are the values for the clean clusters.

The strategy for the analysis of the Pd 3d_{5/2} spectra is the same as for the low-dose experiment. In Fig 5.8 the decomposition of Pd spectra recorded just after
oxidation is shown, with the peak area and BE trends. As with the previous dataset, the violet peaks arise from bulk and surface Pd atoms. The blue and yellow peaks arise from Pd atoms coordinated with oxygen. The main difference from the low exposure experiment is the higher intensity of the high BE component, which also has a larger shift with respect to the bulk component: 1.3 eV, versus 0.8 eV in the lower coverage case.

It may be that this larger shift comes from some contribution from the formation of bulk oxide, certainly present due to the high oxygen exposure, as detected in [12] at oxygen pressures in the mbar regime. Those authors suggest that the bulk oxide component has a shift of about 1.5 eV with respect to the Pd bulk line, close enough to overlap with the 2D surface oxide high BE component observed in our experiment. One problem arising from this interpretation is that the shape of the Pd bulk component (dark violet peak) remains virtually unchanged: if large amounts of bulk PdO were formed this should result in a strong reduction of bulk peak intensity as the yellow peak increases, but the peaks’ area trend shows no change in the three spectra. A possible explanation can be found in [13]. Calculations on TiO$_2$ supported TM clusters exposed to oxygen demonstrate that changes in cluster morphology can occur, as changes in size by a sintering process. If this were the case we should have a decrease of bulk signal caused by oxide formation, as well as an increase caused by the clusters’ growth by sintering, these two effects competing to result in a constant trend of the bulk component. Another possible explanation could be the inhomogeneity of bulk oxide inside the clusters: a partial oxidation could give rise to the new peak, being that the bulk signal is almost unchanged.

It is clear that some further explanations are needed for the yellow peak to justify not only its shift, larger than in the 70 L experiment, but also its intensity trend, which is decoupled from the blue component. The near 1:4 ratio, found in 150°C spectrum, is completely lost in oxidations at 300°C and 400°C, so elevated temperatures must induce modification in the Pd$_5$O$_4$ structure.

In Fig. 5.9 the O 1s spectra multicomponent fit analysis is shown. Here we observe large differences with respect to the low exposure experiment. First of all, the grey component is present in every spectrum of Fig. 5.9, whereas in the low exposure experiment it is absent in the 150°C oxidation. It is surprising that this component is not only present, but even dominates in the 150°C oxidation dataset.

Nevertheless, its monotonically decreasing intensity (with increasing oxidation temperature), is in good agreement with the hypothesis of it being a chemisorbed state, as suggested in ref. [8].

The trends of the blue and yellow components’ intensities are in poorer agreement, even if their BEs are in perfect agreement with the 2D surface oxide components. Assuming the formation of bulk oxide we remember from [8] that this phase contain a component in the O 1s spectrum with a BE very close to the blue peak. The overlap between these two contribution can justify the discoupling between the blue and yellow peaks’ intensities, in agreement with the findings from the Pd 3d analysis.
Figure 5.9. Multicomponent fit analysis of the O 1s spectra recorded after oxidation of the clusters. The violet peak is the Pd 3p\textsubscript{3/2} CL. The trend for peak areas and BEs as a function of oxidation temperature are shown.

In conclusion, the most notable result for this high exposure experiment is the probable formation of a bulk oxide phase, at a much lower oxygen pressure than used in [8]. Another remarkable result is the coexistence of both surface and bulk oxide phases. This interpretation, however, is based on the strong assumption that the high oxygen pressure induces a large change in the cluster morphology, favouring the increase in cluster size. This suggests that in this case XPS investigation alone is not enough to interpret all the features found in the fit.
analysis, and that STM and TEM studies of this system would be very important for a deeper understanding of the system. We do note that the oxidation conditions we used (temperature and $O_2$ pressure and dose) are very similar to Pd single crystal experiments where 2D oxide was observed [6-8], so we can be quite sure that this phase is indeed present. This is a useful point to consider because we have confirmation that the 2D oxide was also observed in the 70 L experiment.

5.1.3 Oxidation at 300°C: a direct comparison between different $O_2$ exposures.

In addition to the data series reported above for 70 L and 600 kL oxygen exposure at 300°C, the same spectra were measured for an intermediate oxygen exposure (3 kL) at the same temperature. We may thus perform a study on the effects of oxygen exposure effects.

![Figure 5.10. Pd 3d$_{5/2}$ and O 1s spectra (superimposed on the Pd 3p$_{3/2}$ line at a BE of 531.7 eV) spectra for different $O_2$ exposure on a sample at 300°C. The black lines are the spectra measured on clean Pd clusters.](image)

In Fig. 5.10 Pd 3d$_{5/2}$ and O 1s spectra for both clean and oxygen exposed nanoclusters are presented. At first glance it appears clearly that small changes occur from 70 L to 3 kL, whereas the successive exposure step strongly influences the lineshape of both Pd 3d$_{5/2}$ and O 1s core level spectra lineshape. To check
these small differences a multicomponent fit analysis was employed, but first it is important to point out qualitative observations, and compare with the corresponding evolution in the C 1s spectra.

![Graph](image1)

**Figure 5.11.** a) Comparison between Pd 3d$_{5/2}$ and O 1s intensity as a function of oxygen exposure. b) Change in C 1s spectrum induced by 600 kL of O$_2$ exposure.

The upper panel of Fig. 5.11 shows the area trends of Pd 3d$_{5/2}$ and O 1s as a function of the O$_2$ exposure. From the clean clusters to those with 70 L exposure the Pd signal decreases sharply as the O coverage rises. The coupling is to be expected: with increasing amounts of oxygen the Pd signal is screened and so its intensity is decreased. This coupling between the two signals vanishes with increasing oxygen exposure: the O 1s intensity grows whereas the Pd signal remains almost constant. The reason for this loss of coupling can be tentatively explained by examining the lower panel. A possible interpretation for the increase in O 1s intensity from 3 kL to 600 kL is the oxygen absorption in CNTs. The variation in C 1s spectrum clearly indicates an interaction between oxygen and carbon nanotubes, detectable only for high exposures. Of course this discrepancy between the Pd 3d$_{5/2}$ and O 1s signals could also be discussed in the context of the aforementioned growth of Pd bulk oxide: the overall Pd signal should remain almost unaffected by the presence of this new oxide phase, whereas the O 1s signal should increase because of the penetration of oxygen atoms in the bulk.
Figure 5.12. Multicomponent fit analysis of the Pd 3d$_{5/2}$ spectra recorded after oxidation of the clusters at 300°C for different oxygen doses. The violet peaks arise from the clean parts of the clusters. The trend for peak areas and BEs as a function of oxygen dose are shown.

We can conclude that this effect in CL spectra should arise from both the bulk oxide formation and the interaction between oxygen and CNTs. These two processes are seen only for oxygen pressures: it is well known that this condition is needed for the formation of bulk oxide [8], which is also the case for oxygen absorption by CNTs, because of their low reactivity.
Figure 5.13. Multicomponent fit analysis of the O 1s spectra recorded after oxidation of the clusters. The violet peak is the Pd 3p$_{3/2}$ CL. The trend for peak areas and BEs as a function of oxygen dose are shown.

From the Pd 3d$_{5/2}$ multicomponent fit analysis we can see that the blue component saturates, whereas the other oxide-induced component, the yellow one, continuously increases in intensity. As stated above, the correct blue/yellow ratio resulting from oxidation of the single crystal surface should be 4:1, from the stoichiometry of the 2D surface oxide (Pd$_5$O$_4$).

This ratio is only obtained in the 3 kL spectrum: the differing ratios at low and high oxygen exposures probably originate from two distinct sources. In the low oxygen exposures the different ratios comes from disorder and the large distribution of geometrical configurations in clusters’ surface. The presence of
undercoordinated atoms could inhibit the completion of the 2D surface oxide layer, leaving the surface oxidation only partly complete, with the ratio between the components arising from other oxygen-coordinated Pd atoms that give a contribution to the blue peak. With increasing oxygen exposure, some of these “blue species” vanish (as seen in the blue peak intensity trend) and a change in cluster morphology occurs, likely introduced by the higher O$_2$ pressure. The ratio 4:1, achieved in the 3 kL exposure, is then exceeded after the 600 kL exposure. This excess is likely related to the overlapping of the bulk oxide component with the yellow peak, as previously stated in high exposure data analysis. The O 1$s$ decomposition shows that the two components arising from the 2D surface oxide have a similar monotonic trend, whereas the supersaturated O$_{ads}$ component is virtually unaffected by the oxygen exposure at this temperature. The oxide components show good BE stability whereas the O$_{ads}$ component undergoes a shift of about 0.5 eV, perhaps induced by the transition from the chemisorbed oxygen to the supersaturated phase. A surprising feature is the behaviour of the violet peak, arising from the Pd 3$p_{3/2}$ core level. Its increase with increasing oxygen exposure is evident also from the rough spectra: the black line in Fig. 5.11, arising from clean Pd clusters, is less intense than spectra measured after the oxidation. This effect is probably another consequence of the change in cluster morphology and of the size increase, favoured by the high oxygen exposure.

5.2 Summary

In conclusion, we have found that several oxide phases are formed on Pd supported nanoclusters, even at low oxygen exposure. The CL analyses for both Pd 3$d_{5/2}$ and O 1$s$ spectra reveal the presence of an oxide phase similar to the 2D surface oxide observed by Lundgren and coworkers in a photoemission study on Pd(111) single crystals. We observe some differences in the components’ BEs, arising from the surface disorder and large distribution of geometrical configurations due to the small size of our particles, composed of about $10^4$ atoms (mean diameter of about 10 nm), as estimated in the previous chapter. The surface defects and low coordination sites probably inhibit the formation of long range surface oxide layers and give rise to the formation of unresolved components in CL spectra, appearing in our analysis as shifts in 2D surface oxide components BEs.

The same oxide phase is formed at higher oxygen exposures, with some deviations from the single crystal behaviour. These differences probably occur because of a change in cluster morphology induced by high oxygen pressure and by the formation of a bulk oxide phase.

The thermal stability of the new oxide phases is higher than was found in the single crystal study. This is not an unexpected result: in [12] the oxygen induced features formed on Pd nanoclusters deposited on Al$_2$O$_3$ also show a higher resistance to annealing, with a thermal limit that increases with oxidation temperature.

Regarding role of the support, the comparison between the Pd 3$d_{5/2}$ and O 1$s$ spectra areas as a function of the oxygen exposure suggests that more oxygen induced features must exist after 600 kL dose. The constant trend of the Pd bulk line excludes the formation of bulk oxide, whereas the change in C 1$s$ spectrum reveals that some interaction between the oxygen and CNTs exists, driven by the high oxygen pressure. It is therefore clear that CNTs act not only as spectators to
the oxidation of Pd nanoclusters at high pressures, but can also play a significant role. Our results, which are based on a long range experimental technique, suggest a modification of the nanoclusters morphology induced by oxygen adsorption not only at the surface, but also in the overall geometry. This point should be better analyzed using other techniques such as Transmission Electron Microscopy (TEM).
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Reference


As previously stated in the introduction of Chapter 4, one of the fastest-developing fields in surface science is research on nanoclusters of semiconducting and metallic materials. The latter have been studied in many different ways: as free clusters, as embedded in a host matrix or as deposited onto a support. The last type is certainly the most relevant for real-world heterogeneous catalysis applications.

A typical supported metal catalyst is usually deposited on a thermally stable and surface-rich oxide support material, such as alumina (Al₂O₃) or silica (SiO₂). On these oxides, well-dispersed metal particles typically in the size range of a few nanometers are prepared via, for example, impregnation of a precursor followed by suitable chemical and thermal treatment (though other methods exist). The role of the support is well described in the literature [1] and is based on several effects. The first is the modification of nanoclusters’ electronic properties induced by the particle-support interactions. The second is the diffusion of the reactants through the surface: this can be classified as either activated (spill over) and non activated (capture zone effect) adsorption.

As usual, our interest lies in model systems. One of the best choices for modelling real oxide-supported catalysts using the surface science approach is the deposition of nanoclusters on an ultra-thin oxide film, which in turn is supported by a conductive material.

The choice of the supported thin films is a compromise between two needs. First of all, we wish to model a real catalyst composed by TM particles supported by a metal oxide. However, performing measurements on metal nanoclusters on a oxide support is non-trivial, because almost all metal oxides are nonconductive. Most surface science experimental techniques (XPS, STM and in general all electron microscopies and spectroscopies) cannot be easily employed if the support is an electrical insulator: the sample undergoes charging, which strongly influences the measurements. Metal oxide thin films represent one solution to this problem. Using an oxide layer of a thickness between 10 and 20 Å, supported by a metal substrate, we obtain two critical desirable characteristics:
• support conductivity: the metal substrate is naturally conductive, and the oxide thin film becomes practically conductive because the reduced thickness opens a significant tunneling channel.
• real oxide behaviour: the oxide layer is thick enough to isolate the surface from metallic substrate influence so the nanocluster support is an almost real oxide.

Of course creating of this kind of oxide/metal support depends critically on the choice of the metal substrate, which must be done in a way so as to match the two lattice constants and to create understandable interactions between the two materials.

The subject of this chapter is the characterisation of the nucleation of Pt nanoclusters on MgO thin films, grown on the (100) surface of a silver monocrystal, and the study of the oxidation of carbon monoxide on these structures.

TM nanoparticle reactivity on MgO thin films has been the subject of intense study in recent years. In [2] a study of bare MgO reactivity with CO was conducted. This is a fundamental work for decoupling the effect of support and the nanoparticles’ chemical reactivity. The DFT analysis clearly shows that there is poor mixing between the frontier orbitals of the adsorbate and the bands of the surface, and that the low adsorption energy is mainly due to weak MgO-CO electrostatic interactions. TDS experiments confirm the low thermal stability of the adsorbate phase: the CO desorption peak is at about 130 K. Other works [3,4] show that this peak is related to CO desorption from defective sites of the MgO surface, whereas the desorption peak arising from the CO bound on a flat MgO terrace is located even lower, at 50 K.

Many investigations have been conducted on MgO supported nanoclusters, focusing on both electronic and structural properties, as well as chemical reactivity. Most of these studies were dedicated to Pd [5-9] and Au [10-12] nanoclusters. Pt clusters have been studied less often than other materials. Heiz et al. [13] have succeeded in the controlled production of size-selected clusters, which allow for a systematic study of their reactivity once deposited onto a chemically inert substrate. In particular they investigated the catalytic reaction of the CO oxidation on platinum and a distinct atom by atom size dependency for monodispersed platinum clusters on thin MgO(100) films has been observed. These results clearly show that the efficiency of a heterogeneous catalytic reaction can be tuned by the choice of particle size.

We performed HRPES measurements for different amounts of Pt, deposited on the MgO(001)/Ag(001) substrate at liquid nitrogen temperature, in order to understand the nucleation mechanism and the morphology of the nanoparticles. After the characterisation of the growth mechanism we performed time-resolved PES measurements during adsorption and desorption of CO on both clean and oxygen pre-covered nanoclusters. This experiment aims to provide us a deeper understanding of the role played by the support and by the clusters’ size in the CO adsorption and oxidation processes. The experiments were performed at different temperatures by monitoring the C 1s and Pt 4f7/2 core levels, which proved to be highly sensitive to the CO-nanocluster interaction.
6.1 Experimental

All the preparation and measurements were done at the SuperESCA beamline of Elettra, previously described in chapter 3. The sample preparation began with the cleaning of the Ag(001) surface by several cycles of Ar⁺ sputtering, at RT and 3·10⁻⁶ mbar pressure, with a beam energy of 1 keV, and annealing to 430°C. After this treatment a sharp (1x1) LEED pattern appeared and XPS measurements revealed a contaminant-free spectrum. The MgO thin film was grown by Mg evaporation in a 1·10⁻⁶ mbar oxygen pressure, with the sample temperature fixed at 230°C, according to the procedure described in [14], wherein the MgO/Ag(001) growth model is well described. The most favoured interface geometry between a metal oxide of rock salt structure and the (001) surface of an fcc metal with similar lattice constants, is such that the metal atoms occupy hollow sites, whereas O atoms occupy top sites. This is in agreement with theoretical and experimental investigations on MgO/Ag(001) growth, and is schematically depicted in Fig. 6.1.

![Diagram of MgO/Ag(001) growth model](image)

**Figure 6.1.** MgO/Ag(001) growth model, schematic illustration of the most favourable configuration: Mg atoms occupy hollow sites, O atoms occupy on top sites. The Ag(001) surface unit cell is indicated.

In the same work further STM and STS analysis reveal that a MgO/Ag(001) thin film’s electronic properties vary from 1 to 3 ML thickness, whereas beyond 3 ML the electronic structure shows no contribution from interface states, but corresponds to the electronic structure of an MgO(001) single crystal surface. This will be a useful information in the calibration of the MgO thin film growth because it states the minimum thickness to obtain.

6.1.1 Determination of MgO overlayer thickness

During the growth of MgO on Ag(001), the Ag 3d₅/₂ peak was measured as a function of the polar emission angle θ. By comparing these spectra to ones collected from clean Ag, we estimated the thickness from the attenuation of the signal. The thickness of the overlayer d was computed for each value of θ by comparing the intensity of the Ag 3d peak after MgO deposition, using the equation
\[ d = \lambda_{MgO}(E)\cos\theta \ln \frac{I_{\text{clean}}}{I_{MgO}} \]

The results are summarized in Fig. 6.2. For MgO the IMFP \( \lambda_{MgO} \) has been calculated using the TPP-2M relation [15], assuming the bulk bandgap value \( E_g = 7.8 \text{ eV}, N_v = 8 \) (6 for oxygen and 2 for Mg), and \( \rho = 3.16 \text{ g/cm}^3 \), from the rocksalt crystal structure (using the 4.2 Å lattice constant).

**Figure 6.2.** Calculation of MgO thickness from attenuation of Ag 3d intensity from spectra collected at \( h\nu = 550 \text{ eV} \). Colours represent different deposition times.

The results from these calculations suggest some photoelectron diffraction effects: there is clearly some systematic dependence of the calculated thickness on the polar emission angle, whereas a constant value for all \( \theta \) values is expected from the TPP-2M model. Nonetheless the average increase of the calculated thickness for angles in the range 40°-50° is typical for square surface lattices. Other measurements performed with higher photon energy show that the calculated thickness is always smaller at larger excitation energies, another possible consequence of the photoelectron diffraction arising from the additional symmetry of the overlayer. However, we may say that for the 4 minute deposition (the one used for the majority of the Pt experiments), the thickness is somewhere between 10–14 Å, which corresponds to 5–7 atomic bilayers of MgO, a reasonable thickness for obtaining the conductivity necessary for XPS measurements.

### 6.1.2 Characterization of Pt nanocluster growth

The Pt evaporator has the same construction and operating principles of the Pd evaporator shown in the previous chapters, and the evaporation was also performed at a constant filament current and with a base pressure of about \( 3 \cdot 10^{-10} \text{ mbar} \). We performed three different depositions on the MgO/Ag sample which was fixed at LN temperature, for 60, 120 and 240 seconds, assuming a constant deposition rate.

It is known that Pt clusters typically grow on MgO with a 3D structure, starting from a (100) base that follows the square surface lattice of the substrate. A recent theoretical work [16] suggests that Pt/MgO clusters optimally manifest with an aspect ratio \( \text{height/diameter} \) of about 0.7 and that their geometry depends on the
number of atoms per cluster \( N \). For \( N < 550 \), (100) growth is more favorable, and above (111) growth is expected. Cluster growth is generally determined by the interplay between surface and adhesion energy, but in the case of the Pt (and also in the limit of large clusters) the difference between the two structures is quite small, as confirmed by the calculations for surface energies on Pt(111) and (100) single crystals [17].

In a previous grazing incidence X-ray scattering (GIXS) analysis [18] the (111) orientation is not observed for clusters grown below 1000 K, a temperature much higher than our hottest annealing temperature of 400°C. Models based on the experimental work for (100) and (111) epitaxy are presented in Fig. 6.3. A section through each illustrates the attenuation of the inner atoms’ contribution to photoemission spectra due to inelastic scattering.

**Figure 6.3.** Schematic models for (100)-oriented (left) and (111)-oriented (right) cluster types grown on MgO(001).

On the basis of these observations we assume that we have (100)-oriented clusters, remembering that the size effects suggested by [16] could arise for high coverages and assuming the calculated aspect ratio is valid.

On a defect free MgO surface, calculations of the Pt-MgO bond reveal that the most stable site of adsorption is the oxygen on-top, with a binding energy of 2.46 eV, whereas the in the Mg on-top position the adsorption energy is 0.55 eV [19]. Similar results are found for an MgO/Ag thin film: the O-Pt bond has exactly the same energy, while the Mg-Pt bond increases in strength to 1.51 eV. However, the nucleation of Pt clusters could also begin from the so called F-centers, oxygen vacancies of the MgO surface, or from steps [20,21]. Indeed, these defected sites, together with the OH groups, are the most reactive of the MgO surface, and have a larger bonding energy with the adsorbed metal, as demonstrated in [22] for Pd nanoclusters.

In Fig. 6.3 is a series of Pt 4f spin-orbit split doublet spectra corresponding to each of the three coverages. Using arguments similar to those made in previous chapters for the evaluation of the coverage we found that the three Pt depositions correspond to approximately 0.03, 0.06 and 0.12 ML. Determination of the cluster size requires a microscopy study, but nonetheless it is known from previous experiments that at these coverages the clusters’ size ranges from \( 10^1 \) to \( 10^4 \) atoms. Assuming the reported aspect ratio and the (100) growth we can say that our clusters’ diameters range from 1 to 7 nm, the heights from 0.7 to 5 nm.

Each dataset consists of 13 spectra collected at increasing annealing temperature, from the deposition at LN to 400°C. As the annealing progresses, we observe that in all the three cases the doublet peaks become narrower, and shift to lower binding energies. We also observe a slight decrease in the overall intensity. If we
assume that the annealing results in the nucleation of clusters, we would expect an attenuation due to screening of atoms internal to these clusters by the outer ones (this is examined in more detail below).

**Figure 6.3.** Pt 4f core level spectra collected for three different coverages, and coloured as a function of anneal temperature.

Every spectrum can be fitted by the same four doublet subcomponents and a linear background, as illustrated in Fig. 6.4. The doublets have identical lineshapes, and are split by 3.28 eV, the expected spin-orbit splitting for the $4f_{7/2}$ and $4f_{5/2}$ core levels. The branching ratio is found to be a single constant throughout the three sets of data.
Figure 6.3. Fitted peak function for all the Pt 4f doublets spectra. The four doublets all share the same lineshape parameters and branching ratio. $C_0$, $C_1$, $C_2$ and $C_3$ are respectively the red, blue, green and yellow components described in the text.

The binding energies of the $4f_{7/2}$ components are reported in Table 1. The shift between the red and the blue component is about 0.6 eV, similar to the size of the SCLS detected on Pt(100) single crystal [23]. This observation is not necessarily a confirmation of (100) growth, despite the fact that it should be more favourable
<table>
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<th>Shift from cluster bulk (eV)</th>
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<td>-0.59</td>
<td>surface/undercoordinated</td>
</tr>
<tr>
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<td>0.0</td>
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<td>C₂ (green)</td>
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</tr>
<tr>
<td>C₃ (yellow)</td>
<td>72.96</td>
<td>+ 2.00</td>
<td>Pt/MgO defects</td>
</tr>
</tbody>
</table>

**Table 6.1.** Details for the sub-components in the fits to the Pt 4f spectra. The binding energies are referenced to the Fermi Level. Assignments of the atom character follow from the analysis in the rest of the document.

at these temperatures, for two reasons. The first is that both (100)- and (111)-oriented clusters will contain both of these surface orientations, albeit with different ratios. The second is that, as reported in [24], the difference between Pt(111) and Pt(100) SCLS is less than 0.1 eV, a shift too small to be resolved in our spectra, because of the peak broadness induced by the reduced size. The only confirmation we have from the presence of this CLS is the presence of a bulk-surface well ordered structure.

Fig. 6.4 shows the area of the 4f\(_{7/2}\) subcomponents, as a function of anneal temperature, plotted on the same intensity scale. For all three coverages we observe similar behaviours that reveal some details of the clusters’ formation mechanism and structure.

**Figure 6.4.** Summary of the trends in the doublets as a function of annealing temperature. The black curve corresponds to the total intensity for the measured data. The individual colors correspond to the intensities from each of the sub-components, as illustrated above.
First of all, the annealing appears to decrease the overall intensity of the Pt 4f signal. This can be attributed either to the Pt atoms desorbing from the surface or, more probably, to screening of the atoms internal to the 3D structure. Another behavior revealed in Fig. 6.4 is the constant value of the C3 intensity. This component dominates at lower coverages, but does not vary in intensity as Pt amount increases. As the preparation method for the MgO films did not vary between experiments, one can assume that the density of F-centers is roughly constant. Thus, it seems reasonable to attribute C3 component to Pt atoms coordinated with MgO defects. Furthermore, C3 is suppressed for annealing temperature, a behaviour consistent with Pt atoms being driven out of the defects to the surface, or possibly being buried and screened by clusters nucleating at these F-centers.

As suggested above, the shift between C0 and C1 may well arise from surface-like and the bulk-like states respectively, most probably with the surface peak comprising an overlap of the (111) and (100) contributions. The last component, C2, probably arises from some 2D small cluster atoms, with high coordination with the MgO support and a few Pt-Pt bonds. This component vanishes at high temperatures and coverages, because these two conditions favour the 3D cluster formation by coalescence.

Every subsequent experiment was performed for each of the Pt coverages after a 400°C annealing in order to ensure that we dealt with well ordered Pt nanoclusters.

6.2 Chemical reactivity

The final aim of this section is the understanding of the CO oxidation mechanism on Pt supported nanoclusters by surveying the C 1s core level during the reaction. Before this step, several preliminary measurements were done in order to study the CO oxidation reaction with sufficient understanding of the individual steps that comprise the reaction during exposure to the molecules in question, i.e. CO and oxygen.

The first step in this preliminary phase of the experiment is the observation of the interaction between CO and bare MgO. The study of this reaction is very important for disentangling the Pt and the MgO contributions to changes induced by CO adsorption in C 1s spectrum.

Another fundamental preliminary experiment is the understanding of the interaction between the Pt single crystal surfaces (111 and 100) and the two species involved in the reaction. Of course, good understanding of the CO oxidation mechanism on Pt single crystal is also useful and completes the background for the experiment.

After the comparison between our results and the literature a discussion will follow, focused on the influence on the CO oxidation of two features: the sample temperature and the Pt coverage.

6.2.1 CO adsorption on bare MgO

Many recent works are focused on the adsorption of CO on several kinds of MgO(001) surfaces, ranging from the single crystal to the thin films grown on both Ag and Mo supports. One of the most relevant studies to our investigation is
Figure 6.5. TD spectra for several CO coverages on MgO single crystal surface. The spectrum in the upper part arises from the saturation coverage, 0.25 ML.

the work of Rodriguez et al. [25]. In this paper MgO CO adsorption capability is compared to intermixed metal-MgO systems, mainly by means of TDS. Focusing our attention on the clean MgO surface, as we can see in Fig. 6.5 the desorption peak arises at about 130 K, even if for higher CO coverage (0.25 ML, in the upper part of the diagram) this peak seems to originate from the overlap of two components. Comparing this result with a previous TDS study [26], where the desorption peak is detected at 60 K, the authors conclude that their 130 K peak must arise from the CO molecules adsorbed on surface defects, whereas the 60 K peak comes from the CO bond to regular surface sites. The calculated binding energies for CO molecule on regular and defective sites are 0.13 and 0.3 eV respectively. This interpretation is in good agreement with the already stated results for metal adsorption on both regular and defective MgO sites: vacancies, steps and other undercoordinated sites produce stronger bonds to adsorbates.

Figure 6.6. CO adsorption on a step on MgO surface. The bond involve two Mg atoms, resulting in a strength increase with respect to the bond on a regular terrace site.
The origin of the higher strength of the defective site bond is depicted in Fig. 6.6, the result of DFT calculations. The diagram depicts the bonding of a CO molecule on a step, where two inequivalent Mg atoms are involved. The Mg$_5$ is the cation laying on a flat terrace whereas Mg$_4$ is the configuration we find on the edge of the step: the double bond on the CO molecule results in a strength increase.

![Diagram](image)

**Figure 6.7.** *TD spectra for CO on MgO/Mo(001) thin film with a 20 ML thickness, before and after annealing.*

A correction to this interpretation comes from another more recent work by Freund and coworkers [27]. Their results are summarized in Fig. 6.7: the TDS study reveals the presence of two peaks, at 52 and 68 K temperature respectively. Also in this case the lower temperature peak is interpreted as arising from the CO molecules desorbing from regular terraces whereas those desorbing from defective sites are identified as the origin of the 68 K peak. The measurement has been performed before and after annealing and the difference between the two spectra confirms this interpretation: the low temperature sites increase after the reordering treatment, whereas the high temperature has the opposite trend. The calculated binding energies corresponding to the two desorption peak are 0.15 and 0.25 eV for regular and defective sites respectively.

Curiously absent in this data is the 130 K peak found in [25]. Even if [25] deals with MgO single crystal and [27] with a thin film grown on Mo(001) substrate, the thickness of the film (20 ML) excludes substrate influences and strong differences between the two surfaces.
After this introduction we can go on with the analysis of our results. CO exposure was performed at LN temperature until saturation. Fig. 6.8 shows the C 1s core level high resolution spectrum. It can clearly be well described by using just two components, $\alpha$ and $\beta$, located at binding energies of 290.9 eV and 292.9 eV, respectively. Both the two components are very broad, indicating that they arise from the overlapping of many unresolved contributions. Nonetheless, the interpretation of this result is clarified with the help of the time-resolved study of the adsorption and desorption, illustrated in Fig. 6.9.

C 1s core level was measured during both CO adsorption and desorption, by the collection of one spectrum every 25 s. The two peaks $\alpha$ and $\beta$ grow almost simultaneously during uptake, though $\beta$ may appear first and is significantly larger after the dose. During temperature-programmed XPS experiments, we also note that $\alpha$ species desorb well before $\beta$ ones (the red spectra clearly show this behavior). Even if this thermal desorption data are not comparable with these
found in [25-27] we can give an interpretation of this result regarding the thermal stability of this two CO phases on the MgO surfaces. By comparison with previous results we attribute the α phase to CO desorbing from regular terraces whereas the stronger bond between β phase and MgO reveals that this peak arises from the CO desorbing from surface defects. The large difference in intensity with respect to the [27] result probably arises from the lower thickness of our MgO film and, as a consequence, the higher defect density. After this first approach to understanding chemical reactivity of the bare MgO a brief analysis of the CO-oxygen interaction will follow.

### 6.2.2 CO oxidation on bare MgO

The main reference is the recent work by Hellmann *et al.* [28], in which the CO oxidation reaction at low temperature is studied by DFT. The simulated system is composed of a slab of two MgO layers both free standing and “grown” on three Ag layers. The results indicate that the activation barrier is lower on bare MgO/Ag(100) than on a Pt(111) single crystal surface, by 0.2 eV, one of the most often used catalysts for this reaction, together with Rh and Pd. Another appealing feature of MgO as a CO oxidation catalyst is that the CO adsorption energy, as shown in the previous section, is low: this assures that CO will not poison the catalyst surface, a typical problem in CO oxidation catalysis at low temperature. On the contrary, the reaction is found to proceed by the Eley-Rideal (ER) mechanism, where oxygen is the adsorbed species reacting with the CO molecule in gas phase. The formation of a CO$_2$ molecule leaves one adsorbed oxygen atom, that may react with another CO to form another CO$_2$ molecule, completing the balanced reaction

$$O^\text{ads}_2 + 2CO^{\text{gas}} \rightarrow 2CO_2^{\text{gas}}$$

The Langmuir-Hinshelwood (LH) mechanism, by which both the reactants are adsorbed species, is here prohibited by the high oxygen coverage with respect to the CO at low temperature. After formation CO$_2$ desorbs and no trace of carbonate formation is detected from calculations. This result is in contrast with a previous experimental finding on the CO-oxygen interaction with MgO by infrared absorption spectroscopy (IRAS) [29]. In this work several absorption bands are attributed to carbonate formation on defective sites, because of their structures to oxygen. The differences between these two works is due to the absence of surface defects in the simulated systems: carbonates are only formed on those sites. Our data on CO-oxygen interaction on bare MgO is limited to CO TDS, performed after CO saturation in an oxygen environment, in a background $O_2$ pressure of about $10^{-7}$ mbar. Fig. 6.10 shows the comparison between TDS in UHV and in O$_2$. As we can see, the presence of the oxygen induce the formation of a new peak in C 1s spectrum, at a BE of about 289.7 eV. This new species, indicated by the blue arrow in the right panel, exhibits a higher thermal stability with respect to the α and β phases and because of its occurrence with oxygen presence we attribute it to the carbonate formation on defect sites.
Chapter 6 – Pt nanoclusters on MgO/Ag(100): growth and chemical reactivity

Figure 6.10. Comparison between CO TDS in UHV (left panel) and in oxygen environment (10^{-7} mbar). The blue arrow indicates the new peak, arising from carbonate-like species, the blue spectra are measured at the same temperature.

A further difference between the two spectra series is the lower thermal stability of β phase when desorbing in oxygen environment. The blue spectrum in left panel is at half of its maximum intensity, whereas in right panel has almost zero intensity. This is probably due to the fact that in oxygen environment CO has two desorption pathways: regular thermal desorption and the reaction with oxygen; this accelerates the desorption rate of the β species.

This concludes the analysis of bare MgO. The comparison between our data and [28] is nontrivial. In our experiment we first saturate MgO with CO and then we react this system with oxygen during the thermal desorption. In [28], instead, the opposite mechanism is used for the oxygen-CO interaction on MgO: an initial adsorption of oxygen that subsequently made to react with gas phase CO. Nonetheless, we have determined how MgO is involved in the CO oxidation mechanism: we can safely begin with the analysis of Pt nanoclusters chemical reactivity.

6.2.3 CO adsorption and desorption on Pt nanoclusters

Platinum is certainly among the most studied transition metal surfaces, and there exists a vast literature dedicated to the interaction of small molecules such as CO and oxygen with Pt.

The adsorption energies for oxygen on (111) and (100) Pt surfaces are reported in [30]. The most stable configurations are the threefold hollow site on the (111) surface, the bridge on the (100), with a BE of 4.6 eV for both sites, which are shown in Fig. 6.11.

On the (111) surface oxygen exposure induces the formation of a p(2x2) ordered structure with a 0.25 ML coverage [31], but for Pt(100) the situation is more complicated. The bare surface reconstructs in a quasi-hexagonal arrangement, even after low temperature annealing. Interaction with oxygen suppresses the reconstruction. The same effect is also found on another surface-phase of Pt(100), the 5x1 reconstruction. Variations in adsorption energies are expected at different coverage, even if the lack of a well defined and stable surface arrangement inhibits a more detailed quantitative analysis.
Adsorption of CO on Pt(111) surface progresses with an interesting behavior: the coexistence of molecules adsorbed on both on-top and bridge sites. In [32,33] the two peaks are observed in C 1s spectra following CO adsorption, separated by 0.7 eV. The binding energies are 286.8 and 286.1 eV for the on-top and bridge states respectively. In Fig. 6.12 is a sequence of C 1s spectra collected during CO uptake at -70°C, with the uptake curves of the total coverage and the separate curves for on-top and bridge sites. One can see that the adsorption starts on the on-top sites, and after an exposure of about 0.5 L bridge-site occupation begins. At saturation a c(4x2) structure is formed, corresponding to a 0.5 ML coverage, equally divided between on-top and bridge sites. The higher intensity detected for bridge adsorption arises from photoelectron diffraction effects. In [34] the adsorption energies are calculated for both the adsorption sites, resulting in 1.36 and 1.14 eV for on-top and bridge respectively, thus showing that on-top configuration is favored.
but toward a more complex configuration. The adsorption energies are similar to those for (111) surface [36], even though the continuous transition from one surface-phase to the another inhibits their precise quantitative determination.

We can now begin with the analysis of our data from CO adsorption and desorption on Pt clusters.

The study was performed by measuring both the C 1s and the Pt 4f/2 CLs as a function of time, though the latter do not yield further information, because of the spectral broadening. For this reason in the following I will focus only on the C 1s spectra.

In Fig. 6.12 we present two sequences of C 1s spectra measured during CO exposure on 0.03 and 0.12 ML Pt coverage clusters. From the previous section we know that the two components contributing to the high BE peak, at about 291 and 293 eV BE in C 1s spectra, arise from CO adsorption on bare MgO. As one might expect, these peaks are not affected by the Pt coverage. However, the other peak, at a BE of about 287 eV, increases in intensity when the coverage is changed from 0.03 to 0.12 ML, clearly indicating that this new component originates from CO adsorbed on the nanoclusters. The BE of this component is very close to the on-top adsorption peak found in [32-33], whereas no trace of the bridge-adsorption peak is found.

![C 1s spectra measured during CO adsorption for 0.03 ML (left) and 0.12 ML (right) Pt coverage after forming nanoclusters.](image)

Figure 6.12. C 1s spectra measured during CO adsorption for 0.03 ML (left) and 0.12 ML (right) Pt coverage after forming nanoclusters.
Figure 6.13. CO/Pt peak intensity and BE shift for 0.03 (left) and 0.12 (right) ML Pt coverage clusters.

In Fig. 6.13 the CO/Pt peak’s intensity (blue) and BE shift (red) as a function of the CO exposure are shown, for both the 0.03 and 0.12 ML of Pt coverage. There is a correlation between these two quantities, that show clear correspondance for the high Pt coverage. For this higher coverage the CO/Pt C 1s component undergoes a 170 meV shift, from the 286.80 eV BE at the beginning of the exposure to the final 286.97 eV value after the CO saturation. A possible explanation of this BE drift with increasing CO exposure can be found in some previous works on CO adsorption on Pt stepped surfaces [37, 38].

Figure 6.14. C 1s spectra for CO adsorption on Pt(322) (upper panel) and Pt(355) (lower panel) surfaces.

In Fig. 6.14 we find C 1s spectra measured during CO adsorption on Pt(322) and Pt(355) surface. These surfaces comprise (111) terraces with (100) and (111)
oriented steps for (322) and (355) respectively. As we can see, several components can be clearly distinguished, even at first glance. On-top and bridge components arise from CO adsorption on (111) terraces, according with previous findings on Pt(111) single crystal, whereas the other components come from the CO adsorption on steps. In Fig. 6.15 the single sites’ occupation evolution during CO exposure is shown. In the right panel two different CO doses on (322) surface are observed by C 1s CL survey: after 0.32 L of CO exposure only the steps’ sites are occupied by adsorbates, whereas larger exposure is required for the population of the terraces’ on-top and bridge sites. In the left panel the uptake curves for each adsorption site on (355) surface are plotted: the adsorption also starts from the step site for this surface (in this case only the on-top adsorption can be detected) and the occupation of terrace sites begin only after saturation of the steps. The step/terrace on-top shift is almost the same for both (322) and (355) surfaces and its value is about 0.25 eV.

**Figure 6.15.** Left panel: CO adsorption on Pt(322) surface for 0.32 L and saturation doses. Right panel: uptake curves for single CO adsorption sites on Pt(355).

On the basis of these results we may reexamine our data and formulate a hypothesis regarding the origin of the shift in CO/Pt peak detected in C 1s spectra during the CO uptake: our clusters have stepped surfaces, with a short range order because of their reduced size. At the start of CO exposure the adsorption begins on step sites and the CO/Pt peak is initially found at 286.8 eV BE. With increasing the exposure, small terraces are populated this shifts the signal toward higher BE. The position we find for the CO/Pt peak at saturation is shifted by 170 meV with respect to the step component: this value, smaller than the 250 meV found for single crystals, arises from the fact that our second signal is the superposition of terrace and step contributions, and not the pure terrace component: the large distribution of inequivalent adsorption sites somehow limits high energy resolution of the apparatus.
A similar analysis was done for the TDS in UHV on the same systems. Figs. 6.16 and 6.17 show the C 1s spectra, the CO/Pt peaks’ intensities and BE shift as a function of the temperature.

**Figure 6.16.** C 1s spectra measured during CO thermal desorption for 0.03 ML (top) and 0.12 ML (bottom) Pt coverage.

**Figure 6.13.** CO/Pt peak intensity and BE shift for 0.03 (left) and 0.12 (right) ML of Pt coverage as function of the temperature.

The trend is symmetric with respect to the uptake findings, revealing that step sites are not only the first to be covered during CO adsorption, but are also those where CO makes stronger bonds.
In conclusion, these two measurements not only yield information on clusters’ interaction with the environment but are also a powerful tool for the investigation of the nanoclusters’ morphology.

The last experiment on the CO/Pt interaction is a temperature desorption measurement in an oxygen atmosphere. As with the bare MgO, we initially saturated the Pt/MgO system with CO and then performed the TDS in an oxygen pressure of $10^{-7}$ mbar. Fig. 6.18 shows a comparison between C 1s spectra measured during the thermal desorption in UHV and in oxygen background.

![C 1s spectra measured during CO thermal desorption in UHV (upper panel) and oxygen (lower panel) atmosphere. The blue arrow indicates the peak arising from the formation of carbonate-like species.](image)

Two effects are observed in the presence of oxygen. The first, already observed on bare MgO, is the formation of a new component, indicated by the blue arrow in the figure. In the CO/MgO interaction analysis we attributed the growth of this new peak to the formation of carbonate species on defect sites of the MgO surface. The BE is similar (290 eV versus the previously found 289.7 eV), so we assume that in this case the new component has the same origin. Nonetheless a peculiar behaviour is manifested by this new feature: its intensity is enhanced by the presence of Pt on the MgO surface. A possible explanation can be found by observing the difference in the CO/Pt component between the UHV and the oxygen desorption measurements. This peak results strongly reduced by the oxygen presence, whereas the CO/MgO peak is largely increased. We can
tentatively attribute the enhancement of the carbonate peak to the activation of CO diffusion processes from Pt clusters to MgO sites, both regular and defects. The experimental findings reported in this section are extremely important for understanding the final part of this investigation: the CO oxidation reaction.

6.2.4. CO oxidation on Pt nanoclusters

As previously reported in section 6.2.2, CO oxidation is one of the most important catalytic chemical reactions and the properties of Pt are widely exploited in many industrially relevant catalysts. In [39] the reaction on Pt(111) single crystal surface is studied by means of HRPES. The study is conducted by surveying the evolution of C 1s spectra during the exposure to CO of oxygen an preadsorbed surface, after the formation of the p(2x2) ordered structure. As expected, bridge sites are inhibited to CO adsorption by the presence of chemisorbed oxygen and CO adsorbs only on on-top sites. As shown in Fig. 6.19, at a temperature of 120 K a 0.23 ML CO coverage is reached, revealing that also some on-top sites must be forbidden by the oxygen pre-exposure (a higher coverage should be reached if all the on-top sites were available). At this temperature no CO oxidation reaction is observed, as revealed by the constant oxygen coverage.

![Figure 6.19. CO exposure of oxygen covered Pt(111) surface at 120 K temperature. On the bridge sites CO adsorption is inhibited by the presence of the oxygen.](image)

A temperature dependent study follows, in the range between 275 and 305 K, to determine the activation energy of the reaction, found to be approximately 0.53 eV. In Fig. 6.20 CO oxidation is observed by the desorption of the oxygen and the consequent activation of the CO adsorption on the bridge sites. The role of CO pressure has been also been examined and the reaction rate increases with increasing pressure up to approximately $1 \cdot 10^{-6}$ mbar. At higher pressures the reaction rate is unaffected.
One of the most important results of this work is the understanding of the roles played by the different oxygen adlayer areas in the kinetics of the reaction. Initially no adsorption of CO is detected, even though a small decrease in oxygen is observed. The small amount of adsorbed oxygen (0.03 ML on the initial 0.25 ML coverage) is attributed to the reaction between the CO and the oxygen adsorbed in disordered structure, outside of the p(2x2) ordered structure. The absence of a regular adsorption pattern makes these species more reactive, thus the reaction with CO is favoured. After this first stage the reaction progresses, but not with the expected first order character: the value resulting from the model is about 0.63. This smaller value of the reaction order is explained by assuming that the reaction involve only oxygen atoms at the edges of the p(2x2) areas, with these species possessing a higher reactivity because of the reduced symmetry. The calculations for a kinetic model involving only edge oxygen atoms results in an order of 0.5, suggesting that this explanation is reasonable.

The CO oxidation on Pt/MgO nanoclusters has been previously studied by Heiz and coworkers [13]. The aim of this work was to demonstrate the cluster size dependence of the chemical reactivity by using size selected clusters ranging from 8 to 20 atoms. As depicted in Fig. 6.21, three different reaction paths result from the TPR analysis. According to single crystal studies, the attribution of these mechanism is the following:

- $\alpha$: CO adsorbed on terrace sites reacts with ionic adsorbed oxygen. This attribution depends on the fact that this phase arises only for larger clusters, where molecular ionic adsorption can be accomplished because of the lower reactivity of fully coordinated Pt atoms.
- $\beta_1$: CO and atomic oxygen are both adsorbed on terrace sites.
- $\beta_2$: CO and atomic oxygen are both adsorbed on step sites.

The $\beta$-phases attribution arise from the similar temperature and pressure conditions used in the Pt(355) single crystal studies and in [13].
The analysis of reactivity as a function of cluster size is depicted in Fig. 6.22. It clearly appears that an important change occurs in the around clusters of 13 atoms: the chemical reactivity is enhanced by 4 times over the critical size. A previous investigation [40] revealed that 13 atoms clusters represent the phase transition from a 2D to a 3D arrangement, and this can explain the trend observed in Fig. 6.22: as clusters arrange in 3D morphology an increase of low coordinated atoms is expected and, as a consequence, the increase of chemical reactivity. After this introduction to CO oxidation reaction on Pt structures we present the analysis of our data.

![Figure 6.21](image1.png)

**Figure 6.21.** Catalytic CO$_2$ formation for different cluster sizes from temperature programmed reaction experiments. Different CO$_2$ formation mechanisms ($\alpha$, $\beta_1$, $\beta_2$) are labeled according to single-crystal studies.

![Figure 6.22](image2.png)

**Figure 6.22.** (a) Total number of catalytically produced CO$_2$ molecules as a function of cluster size. (b) Total number of produced CO$_2$ molecules per atom as a function of cluster size.
In this experiment we studied the influence of temperature and cluster size on the CO oxidation reaction. This was achieved by surveying C 1s spectra during CO exposure at temperatures ranging from -50 to 125 °C, for the three Pt nanocluster nominal coverages (0.03, 0.06 and 0.12 ML). The measurements during the CO exposure (ranging from 1.5 to 2 L) were first performed on clean clusters and subsequently for the same clusters presaturated with oxygen. In Fig. 6.23 the sequence of scans from these two types of experiment is shown, for the large 0.12 ML clusters at -50°C. It is important to remember that both the oxygen pre-saturation and the CO exposure were performed at identical temperatures.

**Figure 6.23. CO adsorption on clean (upper panel) and oxygen presaturated (lower panel) clusters, for 0.12 ML Pt coverage.**

At first glance the main difference between the two measurements is the presence of a new component in the oxygen pre-saturated clusters. This new peak, arising...
between the CO/MgO (high BE) and the CO/Pt peaks (low BE) has a BE similar to the peak induced by carbonate-like species, so we attribute its formation to the same effect detected during the TDS in oxygen environments.

As stated previously, identical measurements were performed for each of the three Pt coverages at several temperatures. The following describes the differences observed between clean and pre-saturated clusters by varying these two parameters. Only the CO/Pt component of the C 1s spectra was considered in this analysis.

In Fig. 6.24 the CO/Pt uptake curves for both clean and oxygen pre-saturated clusters are shown, for each Pt coverage and for two temperatures.

![Figure 6.24. CO/Pt uptake curves for 0.03, 0.06 and 0.12 Pt coverage. The full circles curves are data from the clean clusters, the open circles are data from the oxygen pre-saturated clusters. Both the oxygen and CO exposures were performed at 25°C (left panel) and 125°C (right panel).](image)

The size effect is clear and common to both temperatures: when small clusters (0.03 and 0.06 ML) are pre-saturated by oxygen, the CO coverage does not reach the same saturation point found for clean clusters, whereas for 0.12 ML Pt coverage both the pre-saturated and clean curves reach the same final intensity, even after different CO exposures.

This effect can probably be attributed to the presence of oxygen with a strong bond to Pt. These species are more difficult to remove and CO adsorption barriers in the vicinity of these species are thus higher. The presence of these oxygen species only on smaller clusters indicates they originate from Pt defect adsorption sites, such as undercoordinated atoms or steps, as suggested by previous calculations [41]. This result is unexpected because it is in contrast with the findings of [39], where a higher reactivity was detected for oxygen adsorbed in a disordered manner (as expected to happen on defective sites).
By comparing the 25°C and the 125°C sequences, this interpretation becomes even more convincing. As the temperature increases the difference between the two uptake curves decreases: this confirms that the lack of CO on oxygen pre-saturated clusters is due to the presence of some residual oxygen atoms. Increasing the temperature facilitates desorption of oxygen or even possibly catalytic reaction with CO to form CO$_2$, resulting in the increase of unoccupied adsorption sites.

Figure 6.24. CO/Pt uptake curves on 0.06 Pt coverage cluster for temperature ranging from -50 to 125°C. The black curves arise from the clean clusters, the blue from the oxygen pre-saturated.

Having considered the clusters’ size and coverage effects we may turn our attention to the effect of temperature on the CO oxidation reaction. In Fig. 6.25
the same uptake curves presented in the above analysis are shown for CO/Pt adsorption on 0.06 ML clusters, for all the temperatures. At outset of each of the uptakes we can see that the CO adsorption rate clearly decreases as the temperature increases. This decrease of the CO adsorption rate culminates with the formation of an induction period, a delay in the beginning of CO adsorption, for the 125°C experiment. This temperature induced effect may be explained by one of two distinct arguments. The first is related to the enhancement of the chemical reactivity induced by the temperature. At high temperature CO sticking coefficient is low because CO is more likely instead to react with preadsorbed oxygen than to adsorb on the Pt surface. During this activation period CO₂ formation occurs, while oxygen atoms leave the surface free for CO adsorption. However, since many sites still occupied by oxygen, the adsorption rate remains lower than for clean clusters. We can see this clearly by comparing the derivative of the uptake curve for clean clusters from 0 to 0.1 L with that for the pre-saturated clusters from 0.1 to 0.5 L in the 125°C experiment.

At low temperature the trend is opposite: CO rapidly adsorbs even on pre-saturated Pt surface, whereas small CO₂ amounts are formed. We also notice that the adsorption rate is lower for pre-saturated clusters in this case. The second argument is more complicated and relates to the two possible routes for the arrival of CO on the Pt clusters. A good reference on this topic is [42], even though it deals with Pd clusters on MgO thin films.

The total flux of CO onto the cluster surface is the sum of two available channels for uptake of the molecules, namely direct impingement, and arrival from the bare substrate surrounding, $F_{\text{tot}} = F_{\text{dir}} + F_{\text{diff}}$. Assuming that preadsorbed oxygen inhibits the adsorption of CO we may hypothesize that in the first part of the exposure the uptake of CO onto the clusters is dominated by arrival from the substrate. This process is called reverse spillover and is depicted in Fig. 6.25 by the collection zone model, as illustrated in [42].

![Figure 6.25](image_url)

**Figure 6.25.** The reverse spillover process depicted in the collection zone model, which depends on the mean diffusion length of the molecule on the support at the specific temperature and on the density of clusters [42].

The model assumes that the clusters are regularly spaced on a rectangular grid with lattice parameter $2L$, that every cluster is a perfect sink for CO, and that the system is in a steady state. From the work of Henry *et al.* [43], we may write the expression for clusters of mean radius $R$.
\[
F_{\text{diff}} = 2\pi X_S \alpha J \cdot P \left( \frac{R}{X_S}, \frac{L}{X_S} \right)
\]

where \( P(x,y) \) is a combination of modified Bessel functions, \( \alpha \) is the adsorption probability of CO on MgO, \( J \) is the impinging rate of CO on the surface and \( X_S \) is the mean free path of the molecule on the MgO surface. The arrival rate is simple to calculate from the pressure \( p \), the molecular mass \( M \), and the temperature \( T \) as

\[
J = \frac{p}{\sqrt{2\pi Mk_B T}}
\]

The mean diffusion length \( X_S \) of CO molecules on the MgO substrate can be written analytically as \( X_S = \sqrt{D\tau} \), where \( \tau \), the mean residence time of the CO molecule, is given by

\[
\tau = \nu_a^{-1} \exp \left( \frac{E_{\text{ad}}}{k_B T} \right)
\]

and \( D \), the diffusion coefficient of CO on MgO surface, is given by

\[
D = a_0^2 \nu_d \exp \left( -\frac{E_{\text{diff}}}{k_B T} \right)
\]

In these last two relations \( a_0 \) is the distance between two adsorption sites, \( E_{\text{diff}} \) and \( E_{\text{ad}} \) are the diffusion and adsorption energies, \( \nu_d \) and \( \nu_a \) are the frequency factors for the diffusion and the adsorption process. Focusing our attention only on temperature dependence of \( F_{\text{diff}} \) we find that

\[
F_{\text{diff}} \propto \frac{1}{\sqrt{T}} \exp(1/T)
\]

This results in a decrease of the CO flux onto the Pt clusters as the temperature increases. Starting from the initial assumption, that reverse spillover is the main source of CO flux onto clusters when clusters are pre-covered with oxygen, this can explain the temperature dependence of the delay in the CO uptake: the CO feed rate to the nanoclusters is not large enough to make the uptake begin. However, this interpretation suffers from some problems. The strongest initial assumption is that the system is in a steady state, but during the course of the experiment the CO pressure changes three times, in four steps (1, 2, 5 and 10-10^9 mbar). A second assumption on which the collection model is based is the regular distribution of nanoclusters on the support and we should need some other kind of investigation to make sure of this. Nevertheless this model accounts for the temperature effects we observe in our experimental data and both explanations are reliable.

We conclude by pointing out that the analysis of chemical reactivity’s dependence on temperature is complicated by the fact that, as already said in the introduction, the oxygen exposure has been done at the same temperature of the CO exposure. It is well known that as the temperature changes, oxygen can adsorb on different sites, with different adsorption energies and reactivities. For this reason the
temperature effects are not so simple to interpret, because of the superposition of two contributions.

6.3 Conclusions

The growth of Pt nanoclusters on MgO/Ag support has been characterized by the analysis of the Pt 4f CL, for three different coverages. The interaction of Pt nanoclusters with oxygen and CO has been studied by time-resolved PES, giving us information not only on chemical reactivity but also cluster morphology: by comparing with studies of Pt stepped surfaces we saw that the most favoured facet is Pt(111), and that steps also are present on our clusters. It is worth mentioning that this result was not accomplished by direct observation of the cluster 4f CL, but by the analysis of their interaction with the environment. The interaction between adsorbed CO and oxygen results in the formation of carbonate-like species on MgO defect sites. Curiously, this process is enhanced by the presence of Pt clusters: this probably reveals the presence of a CO diffusion process from clusters to MgO at higher temperatures. CO oxidation has been studied by the surveying the C 1s CL during CO exposure on both clean and oxygen pre-saturated Pt clusters. Both size and temperature effects have been detected. Increasing the temperature results in the decrease of CO adsorption capacity of Pt nanoclusters and this can be explained by one of two arguments. The first is the enhancement of the CO2 formation, which may be more favourable than CO adsorption at the outset of the exposure. The second deals with the reverse spillover, the mechanism by which CO diffuses on the MgO surface towards the Pt clusters. This mechanism becomes slower with increasing temperature, resulting in a decrease of CO supply and, as a consequence, a decrease of the CO uptake. Regarding the size effects: for pre-oxidized small clusters the amount of CO detected subsequent to the exposure is less than for clean clusters. This probably occurs because of the presence of some oxygen species with a strong bond to Pt, leading to a low reactivity with CO.
Reference

Publications


