Computational Study of Nickel Supported on Yttria-stabilized Zirconia

Thesis submitted for the degree of Doctor of Philosophy (PhD) by

Abdelaziz Essadek

Supervised by

Prof. Nora H. de Leeuw

University College London

Department of Chemistry

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Declaration

I, Abdelaziz Essadek, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Abdelaziz Essadek

February 2017
**Abstract**

Solid oxide fuel cells (SOFCs) are an electrochemical device that converts chemical energy by oxidizing fuel into electrical energy. The device consists of three components: the cathode, the electrolyte, and the anode. A common material used for the anode is Ni supported on yttria (Y$_2$O$_3$) stabilized zirconia (ZrO$_2$) (Ni/YSZ). The oxidation of the fuel, e.g. molecular hydrogen, takes place at the anode, at the Ni/YSZ interface.

The performance of the SOFC depends on physico-chemical phenomena, such as Ni sintering, and electrochemical reactions taking place at the triple phase boundary (TPB), where the anode, the electrolyte and the gas phase meet. It is therefore important to understand, at the atomic scale, the microstructure of Ni/YSZ and its interaction with the gaseous phase.

In this thesis, we employ *ab initio* techniques, based on the density functional theory with long-range dispersion corrections (DFT-D2), to investigate the two aspects of the physical chemistry of the TPB: the interaction between Ni and YSZ and the interaction of Ni/YSZ with molecules relevant to SOFC reactions, such as CO$_2$, CO, H$_2$O and H$_2$.

To study those two aspects, we first adsorb one Ni atom on top of both ZrO$_2$ and YSZ surfaces to understand the influence of the Y atom on the Ni adsorption. This provides insight into the preferential adsorption site of the single atom, which allows us to construct Ni clusters supported on both ZrO$_2$ and YSZ surfaces. We proceed by adsorbing clusters of up to 10 Ni atoms, taking into account several configurations and
we study the diffusion of Ni atoms towards neighbouring clusters. We adsorb three molecules (H$_2$O, CO$_2$, and CO) on bare ZrO$_2$ and YSZ surfaces and on the oxide surfaces decorated with one supported Ni atom supported. From this first model, we describe the influence of the dopant and metal atom on the adsorption of the molecule at the TPB. Finally, to determine a more realistic molecule-Ni/YSZ interaction model, we consider several Ni cluster sizes (up to 20) to study the interaction of the CO$_2$ molecule with Ni/YSZ and to determine the influence of the cluster size on the CO$_2$ adsorption. We also evaluate the CO$_2$-H$_2$ co-adsorption on Ni/YSZ to investigate the reverse water gas shift (RWGS) reaction (CO$_2$+H$_2$→H$_2$O+CO), which is one of the reactions taking place at the TPB of the SOFC.
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**List of publications**


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List of conference presentations

2016
• Talk: A. Cadi-Essadek, A. Roldan, and N. H. de Leeuw. A DFT Study of CO$_2$-H$_2$ co-adsorption on Ni/YSZ(111) for Solid Oxide Fuel Cell Applications. **229th ECS meeting. San Diego, CA**
• Poster: A. Cadi-Essadek, A. Roldan, and N. H. de Leeuw. CO$_2$ and H$_2$ interaction with Nickel-Yttria Stablized Zirconia interface: A DFT study. **Cardiff university, Wales**

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Chapter 1

Introduction

Abstract

In this chapter, we give an overview of the solid oxide fuel cell (SOFC), the context of this study, and describe the different materials used in the SOFC components, i.e. cathode, anode, and electrolyte. Among those materials, nickel/yttria-stabilized zirconia is commonly used as an anode, hence our interest in the Ni-oxide interface and its interactions with the gas phase molecules involved in the processes of the SOFC.
1.1 Solid oxide fuel cells – general overview

Nowadays, it is crucial to find another source of energy other than fossil fuels. Hydrogen could be an ideal alternative energy source since it has a high energy density and can be easily adaptable for use in specific device such as Solid Oxide Fuel Cell (SOFC) (Singhal & Kendall 2003).

SOFC is an electrochemical device that converts chemical energy into electrical energy by oxidizing chemical fuel such as hydrogen (Zhu & Deevi 2003). The original idea of the SOFC came from Nernst in 1897, where he proposed a patent describing a solid electrolyte having a thin rod shape that could be electrically conducting, if an external heat is applied to the material, and then kept glowing by the passage of an electric current (Singhal & Kendall 2003). The first conducting materials proposed by Nernst was lime magnesia. More than 100 years later, investigations are still being carried out to improve this original process.

The current SOFC has three main components: two porous electrodes separated by an oxygen ion-conduction electrolyte. We show the schematic view of the SOFC in Figure 1-1, where the operating principle is described. The first step is the reduction of oxygen at the cathode, by the incoming electrons from the circuit, which generates oxygen ions (O$^{2-}$). Then, O$^{2-}$ is transported through the electrolyte towards the anode where it oxidizes fuel such as H$_2$ or CO. Finally, the oxidation of the fuel will generate H$_2$O (and/or CO$_2$) and electrons. The generated electrons migrate to the anode through the external circuit. Therefore, the conversion of the chemical energy into the electrical energy is achieved.
The overall reaction is as follow (Ormerod 2003):

Cathode reaction:

\[ O_2 + 4e^- \rightarrow 2O^{2-} \]  \hspace{1cm} (1-1)

Anode reaction:

\[ H_2 + O^{2-} \rightarrow H_2O + 2e^- \]  \hspace{1cm} (1-2)

\[ CO + O^{2-} \rightarrow CO_2 + 2e^- \]  \hspace{1cm} (1-3)

Total reaction:

\[ H_2 + CO + O_2 \rightarrow H_2O + CO_2 \]  \hspace{1cm} (1-4)

In the SOFC, the electrolyte is solid and the working temperature ranges from 500 to 900 °C, which gives advantages to this power-generating system such as efficiency, reliability, modularity, fuel flexibility, and low pollutants emission (Minh 1993; Singhal 2000b; Yamamoto 2000; Steele 2001; Huijsmans 2001; Gorte 2005; de Bruijn 2005; Kendall 2005; Sun & Stimming 2007; Ormerod 2003; Park et al. 2000; Steele
& Heinzel 2001). The high working temperature of the SOFC allows the use of hydrogen mixed with other gases such as methane and ethane (Fergus 2006).

SOFC can be used at different scales, from small power units to large power plants (Minh 1993; Williams 2001; Singh & Minh 2004; Minh 2004; Cropper et al. 2004), and can convert up to 50% of the chemical energy into the electrical energy (Shri Prakash et al. 2014). One of the most promising application of the SOFC is the residential sector where a combined heat and power (CHP) based on SOFC can be used. In CHP systems, heat and electricity are generated from a single fuel source (Lee et al. 2013). CHP is called micro-CHP when it is applied to small scales such as houses. It is important that both thermal and electrical energies generated by the system match the demand of the residential apartment (Yang et al. 2014). We show the micro-CHP concept applied to a home in Figure 1-2 (Hawkes et al. 2009), where natural gas enters from the gas distribution network and is used by the SOFC to generate heat and electricity. The excess electricity, evaluated thanks to a meter, is exported to the grid while the unused heat is stored in a hot water tank.

![Figure 1-2. Fuel cell micro-CHP concept applied to a home (Hawkes et al. 2009).](image-url)
There are other applications of SOFC such as combined cycle power plant (Choudhury et al. 2013). SOFC can also be applied to military and transport sectors (Choudhury et al. 2013). For instance, Delphi’s SOFC auxiliary power units (APU) has been successfully tested on trucks, Figure 1-3 (Mukerjee et al. 2011).

![SOFC APU](image)

**Figure 1-3.** Delphi’s SOFC APU being tested on a truck (Mukerjee et al. 2011).

The main challenges for the commercialization of the SOFC is the increase of the performance and the reduction of the cost (Choudhury et al. 2013). To reach this goal, investigations are being carried out on different scale: from the cell itself to all the auxiliary systems (Choudhury et al. 2013), Figure 1-4 (Shearing et al. 2010):

![Diagram](image)

**Figure 1-4.** Research and development on SOFC applied to different scales (Shearing et al. 2010).
Our research intervenes in the lowest scale shown in Figure 1-4, i.e. we are interested in the physico-chemical phenomena taking place at the triple phase boundary (TPB) of the SOFC, i.e. the meeting point of the electrode, the electrolyte oxide, and the gas phase. We need therefore to describe, at the atomic scale, the different materials used in the SOFC components (cathode, electrolyte and anode). In Figure 1-5 (Kim et al. 1999), we show a scanning electron micrograph (SEM) of a typical microstructure of SOFC where the cathode, the electrolyte and the anode are identified. In the next section, we give an overview of the different materials used for those three main components.

Figure 1-5. Scanning electron micrograph (SEM) of SOFC showing the microstructure of the cathode (Sr-doped LaMnO$_3$/YSZ), the electrolyte (YSZ), and the anode (Ni/YSZ) (Kim et al. 1999).

### 1.2 Overview of the SOFC components

#### 1.2.1 Cathode

The cathode has to meet the following criteria: high electronic conductivity, chemical and dimensional stability, thermal expansion coefficient matching the other cell
components, compatibility and minimum reactivity with the electrolyte, and sufficient porosity to facilitate transport molecular oxygen from the gas phase to the electrode/electrolyte interface (Singhal 2000b).

Good candidate materials are therefore noble metals and oxides such as perovskite oxides but in practice noble metals are not favoured as they are expensive (Ormerod 2003). One of the most common perovskite used is strontium-doped lanthanum manganite (LSM), $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Lanthanum or strontium cobaltites, $\text{(La,Sr)}\text{CoO}_3$ are also good candidates for cathode materials as they have a high mixed ionic-electronic conduction (Menzler et al. 2010). Additionally, the electrical conductivity of $\text{LaCoO}_3$ is higher than $\text{LaMnO}_3$ (Ormerod 2003). However, at high temperatures $\text{(La,Sr)}\text{CoO}_3$ can react with the yttria-stabilized zirconia (YSZ) electrolyte affecting the performance of the SOFC (Ormerod 2003; Menzler et al. 2010).

1.2.2 Electrolyte

The electrolyte has to be electron insulator but oxygen-ion-conducting and materials such as yttria stabilized-zirconia (YSZ), rare-earth-doped ceria, rare-earth-doped bismuth oxide, and doped lanthanum gallates satisfy this criteria (Singhal 2000b).

YSZ is one of the most common material used as a SOFC electrolyte owing to its high oxygen-ion conductivity, comparing to other materials.

Gadolinium doped ceria (GDC) can also be used as an electrolyte for lower temperatures (550-750°C) (Fergus 2006). Below 600°C, the conductivity of GDC is higher than YSZ. Additionally, GDC is stable with a wider range of cathode materials: lanthanum strontium manganite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM), lanthanum strontium cobaltite
La$_{0.6}$Sr$_{0.4}$CoO$_3$ (LSC), lanthanum strontium ferrite La$_{0.6}$Sr$_{0.4}$FeO$_3$ (LSF), lanthanum strontium cobaltite ferrite La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) (Ralph et al. 2001; Ralph et al. 2003; Qiu et al. 2003; Waller et al. 1996; Dusastre & Kilner 1999). However, GDC is not stable at low oxygen pressure. Perovskite materials can also play a role of a SOFC electrolyte. For instance, doping the LaGaO$_3$ perovskite with strontium and magnesium La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_{y}$O$_3$ (LSGM) allows the material to be oxygen-ion conducting at low-temperature (Joshi et al. 2004). Other perovskites such as LaScO$_3$, LalnO$_3$ and LaYO$_3$ display oxygen-ion conductivity and therefore are candidate for the use as electrolyte materials (Fergus 2006).

1.2.3 Anode

The anode, where the oxidation occurs, has to be stable to face the high working temperature and the reducing atmosphere. Additionally, it must be electronically conducting and must have porosity to maximise the contact area with the fuel (Singhal 2000b). The anode must also be compatible (chemical and thermal expansion) with the electrolyte (Laosiripojana et al. 2009). A common material used as an anode in the SOFC is a porous Ni/YSZ cermet, i.e. a ceramic matrix, here yttria-stabilized zirconia, containing metal (Ni) supported nanoparticles. Ni nanoparticles provide the electronic conductivity, while YSZ provides oxygen-ion conductivity (Graves, Ebbesen & Mogensen 2011; Koide et al. 2000; Ribeiro et al. 2009; Qiao et al. 2007; Muñoz et al. 2006). However, changes of morphology, due to Ni sintering and oxidising, can be observed in the Ni/YSZ, affects the performance of the material. Additionally, Ni/YSZ
is not tolerant to sulfur impurities, which also affects the catalytic performance (Gong et al. 2007; Cheng & Liu 2007; Ebbesen & Mogensen 2009). To overcome this barrier, Ni can be replaced by Cu as Cu/YSZ is more resistant to sulfur impurities (Choi et al. 2007).

Other materials than metal-oxides can also be employed as SOFC anode such as perovskites. For instance, in strontium titanate (SrTiO$_3$), the electronic conduction is achieved thanks to the presence of Ti$^{3+}$ and can be improved by doping the material with tri- or pentavalent oxides such as La$^{3+}$, Y$^{3+}$ and Nb$^{5+}$ (Laosiripojana et al. 2009). However, if a perovskite is used as an electrolyte (e.g. LSGM), instead of YSZ, the diffusion of dopant can take place: for instance gallium or magnesium can diffuse from LSGM electrolyte to SrTiO$_3$ anode (Fergus 2007).

According to the description of the three main components of the SOFC, the choice of the materials is restricted as specific criteria are needed in order to face the high working temperature. Additionally, several physico-chemical phenomena take place at the interface between the different components of the SOFC, which affects the performance of the SOFC. In this project, we focus on the different physico-chemical phenomena occurring at the anode.

### 1.3 Anode materials

Because of the operating conditions of the SOFC, discussed above, a suitable anode material has to fulfil the following criteria (Shri Prakash et al. 2014):

- High electro-catalytic activity towards oxidation of fuel gases
- Preferably a mixed conductor with predominant electronic conductivity to allow the transport of electrons
- Thermal expansion coefficient (TEC) and chemical compatibility with the electrolyte
- Porous structure to permit the fuel and reaction by-products transport
- Fuel flexibility, low cost and ease of synthesis
- Carbon and Sulfur poisoning resistance

The first developed anode materials were single phase such as graphite, platinum group and transition metals (Möbius 1997). However both graphite and platinum group materials do not resist to the rough conditions as the graphite corrodes electrochemically and platinum can be degraded by the water vapour present at the anode-electrolyte interface (Shri Prakash et al. 2014). Concerning the transition metals, Fe, Co, Ni (Jiang & Badwal 1997), Pt (Uchida et al. 1995), and Ru (Suzuki et al. 1993) have been considered for the use as anode material. Among those transition metals Ni has the highest activity with respect to H₂ oxidation (Setoguchi et al. 1992) and is a cheap metal comparing to the other noble metal catalysts such as Pt and Ru (Jiang & Chan 2004; Singhal 2000a). Therefore, Ni was the most attractive transition metal for the use as anode material. Nonetheless, Ni sintering can occur during cell operation, which leads to a possible degradation of the material during the use of the SOFC (Simwonis et al. 2000; Klemensø & Mogensen 2007; Faes et al. 2009; Tanasini et al. 2009; Hanasaki et al. 2014).

The second type of anode material developed were perovskites, such as lanthanum chromite LaCrO₃, which are not affected by carbon deposition (Tsipis & Kharton
Previous studies (Baker et al. 1994; Steele 1999) showed that doping LaCrO$_3$ with alkaline-earth cations ((La,A)CrO$_{3-δ}$ (A=Ca,Sr)) improves the electrocatalytic activity above 426°C. However, the chromites have a low ionic conductivity and their adherence with the electrolyte is not optimum. Other perovskites ((La$_{1-x}$Sr$_x$)Cr$_{0.5}$Mn$_{0.5}$O$_3-x$) have also proven that they can be used as an anode as they facilitate the oxidation of H$_2$ and CH$_4$ at 900°C. Finally, Sr$_{2-x}$La$_x$Mg$_{1-x}$Mn$_x$MoO$_6-x$ materials can also be considered as a competitive material for the SOFC anode (Goodenough & Huang 2007; Huang, Dass, Xing, et al. 2006; Huang et al. 2009; Huang, Dass, Denyszyn, et al. 2006; Kim et al. 2001).

The third family of anode materials is the composite, where two materials are mixed and each of them has a specific role: one is responsible of the ionic conduction and the second material is in charge of the electronic conduction. Ni/YSZ is a popular material used for this purpose due to its electrical, chemical and mechanical properties. Nevertheless, some aspects of this material, such as the poor redox stability, the sulfur poisoning, the carbon deposition due to the use of hydrocarbon fuels, and nickel sintering (Shri Prakash et al. 2014), must be improved. Cu-CeO$_2$-YSZ can be a solution to the carbon deposition where Cu is the electronic conductor and CeO$_2$ the electrocatalyst (Goodenough & Huang 2007; Huang, Dass, Xing, et al. 2006; Huang et al. 2009; Huang, Dass, Denyszyn, et al. 2006; Kim et al. 2001). However, the performance of Cu-CeO$_2$-YSZ is not as optimum as Ni/YSZ (Kaur & Basu 2014). Despite this recent progress concerning the anode materials, Ni/YSZ remains a serious
candidate for high working temperature SOFC due to its properties (Shri Prakash et al. 2014):

- Ni is a good electrocatalyst for the H₂ oxidation and has a high electronic activity (~2x10⁴ S.cm⁻¹ at 1000°C)
- YSZ prevents Ni sintering during operation
- Chemically stable in reducing atmospheres at high temperatures
- Its TEC is close to the common electrolytes used in the SOFC
- Ni does not react with YSZ for a wide range of temperature

1.4 Ni/YSZ and YSZ material structure

The main objective of this thesis is to model the Ni/YSZ interface and its interaction with the molecules involved in the SOFC reactions as the performance of the SOFC depends on the microstructure. It is therefore crucial to describe the crystal structure of ZrO₂ and YSZ bulks, and Ni/YSZ interface.

1.4.1 Zirconia and Yttria stabilized zirconia bulk structure

At atmospheric pressure and below 1400 K, the stable phase of zirconia is monoclinic and it was first described in 1892 by Joseph Baddley. The monoclinic zirconia phase was named in honour to Joseph Baddley and it is called baddeleyite (Xia 2010; Hiemstra 1955). Between 1400 K and 2650 K, zirconia is tetragonal while between 2650 K and 2950 K (polymorph melting point) the most stable phase is the cubic one (c-ZrO₂) (Bogicevic et al. 2001; Aldebert & Traverse 1983). However, when the cubic phase is doped with a cation of lower valence, like Y, it is stabilized at lower
temperatures (below 800 K) and therefore present in the SOFC, in addition to being used in many other catalytic applications (Stefanovich et al. 1994; Guo 2000; Yucai 2005; Wang et al. 2005; Ramaswamy et al. 2004; Dongare et al. 2004; Mercera et al. 1991). Therefore, we will focus on the description of the cubic phase of zirconia in this section.

Cubic zirconia has the fluorite crystal structure: a face centred cubic (fcc) unit cell (space group Fm3m) shown in Figure 1-6. The Zr atoms are arranged in the unit cell to form the fcc cube, each coordinated to 8 oxygen. The position of the O atoms is on the diagonals of the cube.

![Figure 1-6. Crystal structure of cubic zirconia (c-ZrO2). a) and b) represent, respectively, a perspective view and a tetrahedral view of c-ZrO2. Colour key: red and grey spheres correspond to oxygen and zirconium atoms, respectively.](image)

The most common dopant used to stabilize zirconia is c-type Y2O3. The structure of Yttria-stabilized zirconia (YSZ) is a cubic fluorite-like structure, where the yttrium
and zirconium atoms form a face-centred-cubic cation lattice and oxygen and vacancies form a simple cubic anion lattice.

To compensate the total charge, doping zirconia with yttria generates oxygen vacancies as the dopant $Y^{3+}$ has a lower charge than the host $Zr^{4+}$. Indeed, for each $Y_2O_3$ unit introduced in the $ZrO_2$ bulk, one oxygen ion is removed (Bogicevic et al. 2001) (Figure 1-7 from (University of Cambridge n.d.)).

![Figure 1-7](image.png)

**Figure 1-7.** Schematic representation of the introduction of yttria into zirconia (University of Cambridge n.d.).

It has been reported in the literature that the zirconia cubic phase needs to be doped with at least about 8mol% yttria in order to be stable at low temperatures (Ormerod...
2003; Litzelman et al. 2008; Khollam et al. 2001). This is illustrated in the phase diagram of YSZ in Figure 1-8 (Srikanth & Subbarao 1994).

![Phase diagram of YSZ](image)

**Figure 1-8.** Phase diagram of YSZ (m: monoclinic, t: tetragonal, c: cubic) (Srikanth & Subbarao 1994).

The oxygen vacancies generated by the doping allow the oxygen conductivity as the oxygen ions can hop across an edge of a tetrahedron between two cations (Predith et al. 2008). It has been shown that the conductivity of YSZ is maximized for a concentration of dopant of 8-10 mol% Y$_2$O$_3$, then it decreases when more dopant is added into the solid, despite increasing the number of oxygen vacancies (Strickler & Carlson 1963; Dixon et al. 1963; Badwal et al. 2000; Nomura et al. 2000; Ioffe et al. 1978). This decrease of conductivity for a concentration of Y$_2$O$_3$ higher than 8-10 mol% is still unclear and several studies tried to clarify this observation. Two
mechanisms can explain this decrease of conductivity: i) high dopant concentration leads to an increase of the Y-Y interaction affecting the oxygen diffusion as the oxygen diffuses through between two cations ii) the higher the dopant concentration is the more vacancies are present forming an ordered arrangements obstructing the oxygen diffusion into vacant sites (Kilo et al. 2003; Zavodinsky 2004; Litzelman et al. 2008).

After determining the crystal structure of YSZ, we can now describe the Ni/YSZ interface.

1.4.2 Ni/YSZ

The most common synthesis process of Ni/YSZ cermet is the mixing of YSZ and NiO powders following by an in-situ reduction of NiO to nickel metal (Tsoga et al. 1996; Shri Prakash et al. 2014). An example of NiO/YSZ synthesis is described by Kim et al. (Kim et al. 2006) (Figure 1-9):
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Figure 1-9. Synthesis process of NiO/YSZ composite powder (Kim et al. 2006).

The structure of Ni/YSZ can be determined experimentally by using techniques such as X-ray powder diffraction (XRD) as it was achieved by Nahor et al. (Nahor et al. 2014), where the authors deposited Ni film on the YSZ (111) substrate and stated that the most stable orientation is Ni(111)/YSZ(111). They also deposited Ni particles on the YSZ and observed that the metal particles are oriented with the (111) plane parallel to the oxide surface (see Figure 1-10).
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Figure 1-10. High resolution scanning electron micrograph (HRSEM) of a single Ni(111) particle on the YSZ substrate surface. The metal particle is oriented with the (111) plane parallel to YSZ. (Nahor et al. 2014)

1.5 Triple phase boundary (TPB)

In the SOFC, the electrochemical reactions occur at the triple phase boundary (TPB) where the anode, the electrolyte and the fuel meet (Ebrahim et al. 2014; Chen et al. 2004; Zhu & Deevi 2003). Therefore, the performance of the anode depends on the size of the TPB (Bieberle et al. 2001; Goodwin et al. 2009; Lynch et al. 2008).

In this research, we are interested in two aspects of this triple phase boundary: studying the sintering of Ni atoms, which is a parameter that can affect the size of the TPB, and understanding, at the atomic scale, the interaction of the gas phase molecules with Ni/YSZ.

An important parameter to take into account is temperature, as the physico-chemical processes taking place at the TPB depend on this parameter, e.g. sintering. It is therefore important to study the effects of common SOFC working temperatures on
the TPB structure. From DFT calculations, it is possible to extract the relation of certain properties with the temperature, such as the chemical potential, and thus evaluate thermodynamic and kinetic properties. For instance, we will see in chapter 4 that determining the activation energy from DFT allows the calculation of the hopping rate of Ni atoms on top of YSZ as a function of temperature. Other techniques, such as molecular dynamics, can be used to evaluate the sintering of Ni particles on top of the YSZ surface (see next section). Other physico-chemical phenomena, such as the oxygen diffusion within the YSZ bulk, also depend on the temperature and affect the performance of the SOFC. Methods such as microkinetics (see section 1.5.2.) can be used to consider for example atom diffusion within SOFC materials.

1.5.1 Sintering of Ni

Ni sintering reduces the surface of the nickel particles and therefore the electrical conductivity of the anode (Skarmoutsos et al. 2001; Tomoo 1996; Minh 1993). The sintering process is still misunderstood at the atomic scale. Xu et al. (Xu et al. 2013) studied the Ni sintering in the Ni/YSZ anode using molecular dynamics technique and considering the Ni/YSZ structural characteristics: the porosity and the nanoparticle framework. In their study, Xu et al. (Xu et al. 2013) used the Born-Mayer-Huggins (BMH) potential to define the interaction between YSZ atoms. The Ni-Ni interaction was described by the Morse potential. Regarding the Ni-YSZ interaction they employed density functional theory (DFT) to evaluate the interaction energy and fitted Morse potential function to those energies. The authors (Xu et al. 2013) studied two
systems: sintering of two Ni nanoparticles on the YSZ(111) and the sintering of Ni/YSZ multi-nanoparticle. In the first model, they considered 24,030 atoms: two Ni nanoparticles of a 40 Å size and separated by 5 Å on the YSZ(111) surface. The size of the oxide surface was 116.1x100.5 Å². They set up the temperature at 300 K and noticed a sintering of the Ni nanoparticles few hundreds picoseconds after the simulation started. They showed a rotation of the two nanoparticles, towards each other, to facilitate the initial contact point and start a formation of a neck between both particles. Following this first step, Ni atoms from the interior of the Ni particles diffuses towards the neck region which facilitates its growth. Thus, the author showed the importance of Ni atoms diffusion in the process of the sintering. They have also considered two other Ni nanoparticles sizes, 30 Å and 50 Å, and reached the same conclusion meaning that the nanoparticle sizes does not influence the sintering process.

In their second simulations, the authors (Xu et al. 2013) investigated the sintering of the Ni/YSZ multi-nanoparticles in order to take into account the porosity, the framework of the anode material, and the ratio of the Ni to YSZ. Their model, consists of a 100x100x100 Å³ simulation cell containing five Ni and five YSZ nanoparticles with a 40 Å diameter. They considered a temperature of 1073 K and compressed the simulation cell in order to represent the porosity. They showed an aggregation of the Ni nanoparticles. However, this sintering does not take place through small pores in the YSZ framework as those small pores prevent the neck growth between two Ni nanoparticles. Thus, their multi-nanoparticles model describes more realistically the Ni sintering process in the anode material. In their following study (Xu et al. 2015)
the authors compared the Ni sintering in YSZ and ScSZ and observed that the Ni aggregation is more important in Ni/YSZ as the Ni-YSZ adhesion is weaker comparing to Ni-ScSZ. They have also showed that the Ni sintering affects the size of the TPB for both systems.

1.5.2 Reactions at the TPB

During the operation of the SOFC, the oxidation of H$_2$ molecule takes place at the Ni/YSZ anode (Ammal & Heyden 2012; Bessler 2005; Bessler et al. 2007; Vogler et al. 2009; Rossmeisl & Bessler 2008; Bieberle & Gauckler 2002; Goodwin et al. 2009; Anderson & Vayner 2006; Ingram & Linic 2009; Bieberle et al. 2001; Hansen et al. 2004; Sukeshini et al. 2006; Grgicak & Giorgi 2007). The H$_2$ oxidation process was still in discussion and a reliable and accurate ab initio techniques is needed to understand this process at the atomic scale.

Recently, DFT have been employed to examine the H$_2$ oxidation at the Ni/YSZ interface (Shishkin & Ziegler 2009; Shishkin & Ziegler 2010; Cucinotta et al. 2011). In their first investigation, Shishkin et al. (Shishkin & Ziegler 2009) considered 18 Ni atoms supported on YSZ slab with 9% mol concentration of yttria. The YSZ slab consists of nine atomic layers (twelve ZrO$_2$ formula units, i.e. 36 atoms). They used the most stable surface which is the (111) and to satisfy the 9% mol concentration of yttria they replaced two Zr atoms (from the second and the forth atomic layer) by two Y atoms and removed one oxygen from the third atomic layer. The bottom three layers were kept fixed while the rest of the atoms were allowed to move. Before adsorbing the Ni cluster, they extended the YSZ surface to two units. The Ni cluster consists of
three layers: nine, six and three atoms for the bottom, medium and top layer, respectively. In this study, the authors also considered the oxygen-enriched YSZ (YSZ+O), an oxygen fills the YSZ vacancy, as they assume that there is an oxygen transport from the bulk to the surface where the oxidation of the fuel takes place. This YSZ+O surface is detailed in their previous study (Shishkin & Ziegler 2008). In (Shishkin & Ziegler 2009) the authors stated that H\textsubscript{2} prefers to adsorb on the Ni cluster rather than on the YSZ or YSZ+O surface of the cermet. A possible mechanism of H\textsubscript{2} oxidation on Ni/YSZ+O cermet is a dissociative adsorption of H\textsubscript{2} followed by spillover to react with an oxygen surface and form water molecule. In the case of Ni/YSZ+O cermet, both hydrogens react with the additional oxygen atom to generate water molecule. In the Ni/YSZ cermet, the hydrogens react with an oxygen located at the interface between the oxide and the Ni cluster (Shishkin & Ziegler 2010) (Figure 1-11). Another possible pathway is an oxidation of H\textsubscript{2} on Ni cluster after a spillover of an oxygen from the oxide surface.

Figure 1-11. H\textsubscript{2} oxidation at the Ni/YSZ interface (Shishkin & Ziegler 2010). Colour key: O, Zr, Y, and Ni are respectively represented by a red, grey, green, and blue sphere. The white sphere corresponds to H.
However, the overall H\textsubscript{2} oxidation process presented in Shishkin’s investigations (Shishkin & Ziegler 2009; Shishkin & Ziegler 2010) is endothermic, which is in disagreement with the requirements for the operation of the SOFC, as it was pointed out by Cucinotta et al. (Cucinotta et al. 2011). Indeed, the overall H\textsubscript{2} oxidation at the TPB must be exothermic.

Cucinotta et al. (Cucinotta et al. 2011) modelled the TPB by a larger model where they created a Ni cluster atom (46 atoms) exposing the (111) surface and supported on the (111) YSZ surface (219 atoms) containing 9 atomic layers and 8.7 mol\% of yttria (Figure 1-12).

![Figure 1-12. Model of the Ni/YSZ from (Cucinotta et al. 2011). Colour key: O, Zr, Y, and Ni are respectively represented by a red, grey, green, and blue sphere. The yellow sphere corresponds to the oxygen vacancy. O\textsubscript{int} and O\textsubscript{bulk} correspond to the interface and bulk O atoms, respectively, involved in the oxidation process.](image)
The H$_2$ oxidation at the TPB is due to an oxygen atom at the interface between the metal cluster and the oxide surface. The authors described few configurations where the overall reaction is exothermic. The most favourable pathway discussed in this investigation starts with a dissociative chemisorption of H$_2$ on Ni cluster followed by a spillover of H from Ni to an oxygen at the Ni/YSZ interface. The oxygen at the interface will therefore be bridged to Ni and the vacancy left by this oxygen will be filled by an oxygen coming from the bulk of the slab. Then, the second hydrogen will migrate towards OH to generate water. The last step is the desorption of water. The rate limiting step of this process is the H spillover from Ni to YSZ. The authors have also considered the spillover of an oxygen towards the adsorbed H but this pathway was energetically less favourable.

Ammal et al. (Ammal & Heyden 2012) combined (DFT) and microkinetic to model the H$_2$ oxidation at the Ni/YSZ interface. The model adopted in this investigation consists of 18 Ni atoms cluster supported on 9 atomic layers YSZ slab (Zr$_{40}$Y$_8$O$_{92}$, 8.3 mol% of yttria), similarly to the study made by Shishkin et al. (Shishkin & Ziegler 2009; Shishkin & Ziegler 2010). Ammal et al. (Ammal & Heyden 2012) implemented the DFT-derived parameters (e.g. reaction energies, activation barriers, and frequency factors) in their microkinetic model in order to evaluate the H$_2$ oxidation under the experimental conditions. Their overall H$_2$ oxidation process is similar to Cucinotta et al. (Cucinotta et al. 2011). However, Ammal et al. (Ammal & Heyden 2012) also took into account the overall oxygen migration process: i) Oxygen migration from the bulk to the surface oxygen vacancy leading to a creation of a vacancy in the bulk, ii) an oxygen from the electrolyte fills the oxygen vacancy created in the YSZ bulk, and iii)
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reduction of oxygen at the cathode-electrolyte interface in order to fill the vacancy created in the electrolyte. From their report, the authors concluded that the bulk oxygen diffusion is the rate limiting step at lower temperatures (<1000 K) and only at high temperatures (>1000 K) the H spillover becomes rate limiting.

Another possible gas phase molecule interaction with Ni/YSZ is the adsorption of sulphide (H₂S) at the Ni/YSZ interface. Indeed, the fuel used in the SOFC, such as syngas (synthesis gas, e.g. H₂/CO gas mixture) derived from coal (Trembly et al. 2006), can contain a small amounts of sulfur contaminants (Cheng & Liu 2007; Y. Matsuzaki & Yasuda 2000; Trembly et al. 2006; Zha et al. 2007). The adsorption of sulfur at the anodes affects the performance of the SOFC as it blocks the active sites of the device (Cheng et al. 2011; Bartholomew et al. 1982).

Previous investigations (Wang & Liu 2007; Alfonso 2008; Monder & Karan 2010; Malyi et al. 2013) stated that H₂S adsorbs strongly on a nickel surface but, as it is stated by Zeng et al. (Zeng et al. 2013), this is not concluding as it does not explain the higher resistance, of other anodes such as Ni-ScSZ, to sulfur comparing to Ni/YSZ (Sasaki et al. 2006; Hagen et al. 2011; Aravind et al. 2008; Zhang et al. 2010). Thus, in Zeng et al. (Zeng et al. 2013) used DFT technique to study the sulfur adsorption on Ni atoms at the TPB of Ni/YSZ. However, they decided to consider those later atoms in their DFT calculations in order to determine a trend concerning the effect of the dopant radius on the sulfur adsorption at the TPB. For Ni/YSZ, they considered a similar model as the one used by Shishkin et al. (Shishkin & Ziegler 2009) and to construct Ni/XSZ they used the same model and the only difference is in the optimized
position of the $X^{3+}$ atom and O vacancy. They have concluded that the sulfur adsorption is stronger for larger $X^{3+}$ radius. This is due to the influence of the $X^{3+}$ radius on the XSZ surface energy: for large $X^{3+}$ radius, the surface energy is lower. The straightforward consequence is a better adhesion of Ni clusters on XSZ. Thus, the stronger Ni-XSZ interaction, for larger $X^{3+}$ radius, weakens the Ni-sulfur interaction explaining the better resistance to sulfur poisoning for those large size dopants.

A possible way to eliminate the adsorbed sulfur at the anode is to oxidize it by $O_2$ and $H_2O$ to generate $SO_2$ (Chu et al. 2014). However, $SO_2$ molecule is a pollutant as it can interact with air to generate acidic rains which are responsible of the corrosion of metals and deterioration of stone buildings (Stern et al. 1997). Thus, Chu et al. (Chu et al. 2014) used DFT method to study the interaction of $SO_2$ with both YSZ and YSZ+O surfaces. In their model, they considered the same surfaces as the one in ref (Shishkin & Ziegler 2009). They showed that there is a strong interaction between $SO_2$ and both YSZ and YSZ+O surfaces leading to a formation of surface $SO_3^{2-}$ and $SO_4^{2-}$ species (the latter only on YSZ+O surface). Thus, $SO_x$ species ($x=$2-4) are responsible of the YSZ surface poisoning and this poisoning is more important on the YSZ+O.

1.6 Solid oxide electrolyser cell (SOEC)

SOFC can also be used as an electrolyser, which is the reverse mode of the SOFC. In this mode, the name of SOFC changes into solid oxide electrolyser cell (SOEC). Thus, the Ni/YSZ anode in the SOFC plays a role of the cathode in the SOEC. Zhan et al. (Zhan et al. 2009) showed that SOFC can be used as SOEC, with Ni/YSZ as electrode,
to produce syngas ($\text{H}_2/\text{CO}$) through $\text{H}_2\text{O}/\text{CO}_2$ co-electrolysis. Therefore, greenhouse gas such as $\text{CO}_2$ can be transformed into a fuel like syngas (Cinti et al. 2016; Fu et al. 2010; Graves, Ebbesen, Mogensen, et al. 2011). The generated syngas may be transformed, through subsequent reactions, into methanol or other liquid hydrocarbon fuels (by Fischer-Tropsch process) that will be used in a renewable energy cycle. For instance, the final liquid fuels obtained from the conversion of the syngas, can be used in the transportation sector without changing the existing infrastructure and motor engine technology (Fu et al. 2010).

Fu et al. (Fu et al. 2010) demonstrated computationally that the energy conversion efficiency of steam/$\text{CO}_2$ into $\text{H}_2/\text{CO}$ is around 87-93% which is 10-15% higher than a low-temperature water electrolyser system. The authors also showed that producing synthetic fuels, through SOEC, can be economically competitive comparing to the biomass to liquid process: overall fuel production would cost around 0.86 €/l which is in the range of the price of fuel production through the biomass to liquid process.

In (Figure 1-13) we show the operating principle of the SOEC (Fu et al. 2010):

![Figure 1-13. Principle of the co-electrolysis of steam/$\text{CO}_2$ in the SOEC (Fu et al. 2010).](image)
An external voltage is applied to the SOEC which allows the transport of oxygen ions (O\textsuperscript{2-}) from the cathode (e.g. Ni/YSZ), through the electrolyte (e.g. YSZ), to the anode (e.g. La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}/YSZ) where O\textsuperscript{2-} is oxidized to O\textsubscript{2}. There is a reduction of both H\textsubscript{2}O and CO\textsubscript{2} at the cathode which generates H\textsubscript{2} and CO, respectively. The overall reaction can be written as follow (Fu et al. 2010):

Cathode reaction:

\[
H_2O + 2e^- \rightarrow H_2 + O^{2-} \quad (1-6)
\]

\[
CO_2 + 2e^- \rightarrow CO + O^{2-} \quad (1-7)
\]

Anode reaction:

\[
O^{2-} \rightarrow \frac{1}{2}O^{2-} + 2e^- \quad (1-8)
\]

Total reaction:

\[
CO_2 + 2H_2O \xrightarrow{Electricity+Heat} CO + 2H_2 + \frac{3}{2}O_2 \quad (1-9)
\]

The main advantage of the co-electrolysis occurring in the SOEC is its endothermic characteristic. Indeed, the reactions in the SOEC take place at high temperatures meaning that heat can be provided to the device by reaction losses (Joule heat) or by an external source (industry waste heat, concentrated solar, renewable electrical energy, or nuclear power) (Rinaldi et al. 2015; W. Li et al. 2013). Additionally, as the reactions happen at high temperatures, the reaction kinetics are fast and therefore there is no need for an extra catalyst.

However, because of the high working temperature of the SOEC, other reactions such as the reverser water gas shift (RWGS) reaction (equation (1-11)) can take place at both electrodes (Fu et al. 2010). The RWGS reaction occurs at the Ni/YSZ electrode.
and it has been stated that the conversion of CO$_2$ into CO could be achieved through the RWGS reaction instead of the electrode chemical CO$_2$-reduction (reaction (1-7)) (Fu et al. 2010; Dalgaard Ebbesen et al. 2009).

$$CO_2 + H_2 \rightarrow CO + H_2O$$ (1-11)

1.7 Objectives of the thesis

In this chapter 1, we have seen that the characteristics and performance of the SOFC depends on the microstructure of the electrode/electrolyte material, e.g. Ni/YSZ, and its interactions with gas molecules intervening in the electro-chemical reactions. It is therefore crucial to understand at the atomic scale all these physico-chemical phenomena to improve the efficiency of the device.

The main goal is then to understand the geometric and electronic structures of Ni/YSZ interface and its interaction with the gas phase, i.e. the molecules involved in the reactions of the SOEC. The strategy of this investigation starts with choosing the appropriate method to study the TPB at the atomic scale. In chapter 2, we introduce the methodology used to perform our calculations, i.e. DFT. We describe the equations behind this technique and the model used to study the TPB. In chapter 3, we investigate the adsorption of one single Ni atom on top of ZrO$_2$(111) surface and on surfaces with two concentrations of yttrium. This first step provides insight into the preference of Ni adsorption on those oxide surfaces, which indicates the way to construct Ni cluster on ZrO$_2$(111) and YSZ(111). In chapter 4, we describe the adsorption of Ni$_n$ (n=1-10) clusters on the ZrO$_2$(111) and YSZ(111) surfaces in order
to understand the Ni aggregation on top of the later surfaces. We discuss the different cluster geometries and determine the electronic structure of the most stable configurations. In chapter 5, we focus on the interaction of four surfaces (ZrO$_2$(111), Ni$_3$/ZrO$_2$(111), YSZ(111), and Ni$_1$/YSZ(111)) with three molecules present in the SOFC, i.e. H$_2$O, CO$_2$, and CO. We study several configurations and analyse the geometries, the electronic structure, and the vibrational modes of the most stable adsorption sites. In chapter 6, we analyse the interaction of CO$_2$ with the clean YSZ(111) surface and with Ni$_n$/YSZ(111) (n=1, 4-7, 10, 20) interfaces where several adsorption sites and orientations of the CO$_2$ molecules are considered. This allows us to understand the influence of the Ni cluster size on the adsorption of small molecules such as CO$_2$. In chapter 6, we also consider the RWGS reaction at the Ni/YSZ interface.
Chapter 2

Computational methods

Abstract

In this chapter we describe the theory and methodology adopted to obtain the results of this investigation. To study our system, we have used the density functional theory (DFT) which is an approximation to solve the Schrödinger equation. It is accepted that DFT calculations are able to reproduce accurately the electronic and geometric structures of periodic solids. In this thesis, we have solved the DFT equations for our materials using the Vienna Ab-initio Simulation Package (VASP).
2.1 Introduction

The aim of this chapter is to introduce the methods and techniques that have been used in this thesis. As we are interested in describing the electronic and geometric structures of bulk materials, their surfaces and interfaces we have chosen the density functional theory (DFT) (Hohenberg & Kohn 1964) approximation. This is an ab-initio quantum chemistry method where the Schrödinger equation is solved using the electronic density as a functional. DFT has proven its suitability for describing materials properties at the atomic scale thanks to its predictive power, providing results in close agreement with experiments. We have used the Vienna Ab-initio Simulation Package (VASP) (Kresse & Hafner 1993; Kresse & Hafner 1994; Kresse & Furthmüller 1996a; Kresse & Furthmüller 1996b) which is a plane-wave basis set DFT code.

In this section, we present a summary of the DFT theory, where we describe the equations used by this method. First, we introduce the time-independent nonrelativistic Schrödinger equation and the Born-Oppenheimer approximation which defines the motion of many electrons in a field of static nuclei. Then, we explain the Hohenberg-Kohn theorems and their implementation in the Kohn-Sham equations. We also discuss the methodology used to describe the long-range dispersion interactions. We detail the geometry optimization techniques adopted to investigate our material. Finally, we outline the different techniques employed to characterize our material and the interfaces: Bader charge analysis, density of states (DOS), electron localization function (ELF), vibrational frequencies and transition state theory (TST).
2.2 The Schrödinger equation

The nonrelativistic quantum description of a many body system consists in solving the Schrödinger equation. Considering a chemical system composed of M nuclei and N electrons, described respectively by the coordinates \( R = R_1, ..., R_M \) and \( r = r_1, ..., r_N \), the Schrödinger equation can be written as:

\[
\hat{H}\Psi(r, R) = E\Psi(r, R) \tag{2-1}
\]

where \( \hat{H} \) is the time-independent Hamiltonian operator and \( \Psi(r, R) \) is the wave function representing a state with finite energy \( E \). The expression of the Hamiltonian is given as:

\[
\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{NN} \tag{2-2}
\]

where \( \hat{T}_e \) and \( \hat{T}_N \) are the kinetic energy operators of the electrons and nuclei, respectively and are described by equations (2-3) and (2-4) respectively.

\[
\hat{T}_e = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 \tag{2-3}
\]

\[
\hat{T}_N = -\sum_{i=1}^{M} \frac{1}{2M_i} \nabla_i^2 \tag{2-4}
\]

where \( M_i \) corresponds to the ratio of the mass of nucleus \( I \) to the mass of an electron \( i \). The Laplace operator (\( \nabla \)) corresponds to the second derivative with respect to the spatial coordinates of the nucleus or electron.
\( \hat{V}_{eN}, \hat{V}_{ee} \) and \( \hat{V}_{NN} \) represent the potential energy operators for the electron-nucleus interaction, electron-electron interaction, and nucleus-nucleus interaction, respectively. The form of these operators is shown in equations (2-5), (2-6), and (2-7):

\[
\hat{V}_{eN} = -\sum_{i=1}^{N} \sum_{l=1}^{M} \frac{Z_l}{r_{il}} \tag{2-5}
\]

\[
\hat{V}_{ee} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{r_{ij}} \tag{2-6}
\]

\[
\hat{V}_{NN} = \sum_{l=1}^{M} \sum_{j=l}^{M} \frac{Z_l Z_j}{R_{IJ}} \tag{2-7}
\]

The three above operators are given in atomic units and \( r_{ij}, r_{il}, \) and \( R_{IJ} \) are the \( i^{th} - j^{th} \) electrons, \( i^{th} \) electron-\( l^{th} \) nucleus, and \( l^{th} - J^{th} \) nuclei distances, respectively. \( Z_l \) and \( Z_j \) are the atomic numbers of nuclei \( l \) and \( J \), respectively.

Solving equation (2-1) provides all the physical and chemical properties of our system. However, in a system with \( M \) nuclei and \( N \) electrons interacting, the equation is too complex to be solved without considering any approximation.

One possible approach towards solving the Schrödinger equation is the Born-Oppenheimer approximation (Born & Oppenheimer 1927). This approximation separates the electron from the proton variables as their mass ratio is 1:1836 and the electron and nuclei movements can therefore be considered as independent. The Born-Oppenheimer approximation considers the nuclei being in a static position where the electrons move faster than the nuclei due to their very low mass. This approximation
neglects the kinetic energy of the nuclei $\hat{T}_N$ and considers the nuclei repulsion $\hat{V}_{NN}$ as constant. The equation becomes simpler as only the $N$ electrons moving in an external constant potential generated by the static $M$ nuclei are considered. The resulting simplified Hamiltonian is named electronic Hamiltonian $\hat{H}_el$:

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee}$$  \hspace{1cm} (2-8)

Despite this significant simplification, it is still difficult to solve the above equation because of the last term ($\hat{V}_{ee}$). Thus, equation (2-8) has exact solution only for the hydrogen-like atoms (nucleus of any size and a single electron) and further approximations are required for multi-electronic or poly-atomic systems. In the case of solid state modelling, the density functional theory (DFT) is the usual method of choice to evaluate the $\hat{V}_{ee}$ term.

### 2.3 Density functional theory

#### 2.3.1 The Hohenberg-Kohn theorems

The density functional theory (DFT) considers the electronic density of the system to solve the Schrödinger equation. Hohenberg and Kohn in 1964 proved that for any chemical system the energy is a function of its electronic density, which lead them to formulate the following theorems (Hohenberg & Kohn 1964):

“Any observable magnitude of a stationary non-degenerated groundstate can be calculated exactly from its electronic density.”

“The electronic density of a stationary non-degenerated groundstate can be calculated exactly determining the density that minimizes the energy of the ground-state.”
Based on these theorems, the total energy \( E[\rho(r)] \) of the system can be reformulated as a function of the electronic density \( \rho(r) \) :

\[
E[\rho(r)] = \int V(r)\rho(r)dr + F[\rho(r)] \tag{2-9}
\]

where \( V(r) \), for atomic systems, is the coulomb attraction between nuclei and electrons. \( F[\rho(r)] \) represents the kinetic energy, the inter-electronic coulomb repulsion, the exchange and the correlation energies.

The variational principle is employed to minimize \( E[\rho(r)] \) and to obtain the ground state energy of the system and the exact \( \rho(r) \). However, the determination of the total energy as a function of the electronic density is still difficult due to the electron-electron repulsion term (equation (2-6)) in the Hamiltonian. Kohn and Sham (Kohn & Sham 1965) proposed a solution to find the solution of \( E[\rho(r)] \).

### 2.3.2 The Kohn-Sham equations

The development of the density functional theory came from the concepts proposed by Kohn and Sham (Kohn & Sham 1965). Kohn and Sham proved that a fictitious system of non-interacting electrons has the same density as the real system of interacting electrons, which energy \( E[\rho(r)] \) can be expressed as follow:

\[
E[\rho(r)] = T_e[\rho(r)] + V_{el}[\rho(r)] + V_{ee}[\rho(r)] + E_{xc}[\rho(r)] \tag{2-10}
\]

where \( T_e[\rho(r)] \), \( V_{el}[\rho(r)] \), \( V_{ee}[\rho(r)] \) and \( E_{xc}[\rho(r)] \) correspond to the kinetic energy of the non-interacting electrons, the nuclei-electron interaction, the inter-electronic repulsion and the exchange-correlation energy, respectively. However, the kinetic
energy from equation (2-10) is different from the real system. Thus, the correction to this difference is included in the exchange-correlation term along with the exchange energy, correlation energy and the auto-interaction correction. To solve equation (2-10), the energy \( E[\rho(r)] \) is expressed in terms of the one-electron orbitals \( \psi_i \):

\[
E[\rho(r)] = \sum_{i=1}^{N} \left\langle \psi_i \left| -\frac{1}{2} \nabla^2 - \sum_{A=1}^{M} \frac{Z_A}{|r - R_A|} + \frac{1}{2} \int \frac{\rho(r')}{|r - r'|} \, dr' \right| \psi_i \right\rangle + E_{xc}[\rho(r)]
\]

where \( \rho(r) \) is expressed as:

\[
\rho(r) = \sum_{i=1}^{N} |\psi_i|^2
\]

The one-electron orbitals are defined by the Kohn-Sham equation:

\[
\hat{h}^{KS} \psi_i = \left[ -\frac{1}{2} \nabla^2 - \sum_{A=1}^{M} \frac{Z_A}{|r - R_A|} + \frac{1}{2} \int \frac{\rho(r')}{|r - r'|} \, dr' + V_{xc}(r) \right] \psi_i = \epsilon_i^{KS} \psi_i
\]

where \( V_{xc}(r) \) corresponds to \( \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \).

This equation is solved iteratively, i.e. self-consistently, by providing an initial guess to the electronic density of equation (2-10) which returns the energy to be used in equation (2-13) and a new density through equation (2-12). Nevertheless, the form of the exchange-correlation term \( E_{xc}[\rho(r)] \) is not exact and further approximations are needed.
2.3.3 Exchange-correlation functionals: LDA and GGA

In this section, we discuss two methods that are used to evaluate the exchange-correlation term $E_{xc}[\rho(r)]$: i.e. the local density approximation (LDA) and the gradient generalized approximation (GGA).

In the LDA, the density is treated locally and the exchange-correlation energy is calculated as:

$$E_{xc}^{LDA} = \int d^3r \rho(r) \varepsilon_{xc}^{LDA}(r)$$  \hspace{1cm} (2-14)

where $\varepsilon_{xc}^{LDA}$ is the exchange-correlation energy per particle of a uniform electron gas.

Different functionals have been developed within the LDA, such as the widely studied Vosko, Wilk and Nusair (VWN) (Vosko et al. 1980) implemented following the interpolation of correlation energies values from Monte-Carlo calculations.

The exchange-correlation energy from the LDA provides satisfactory geometries, vibrational frequencies and charge densities for metals, where the density is uniform. However, results from this approximation worsen for other cases, such as the overestimation of the binding energy.

For spin polarized calculations, the LDA-based local spin density approximation (LSDA) treats independently the alpha and beta spin channels.

The generalized gradient approximation (GGA) represents an improvement to evaluate the exchange-correlation energy. The GGA considers the variation of the electronic density at the integration point (as in the LDA method) and its surroundings.
Thus, by including the gradient of the electronic density $\nabla \rho(r)$, the non-local effects are introduced on the GGA exchange-correlation energy:

$$E_{xc}^{GGA} = \int d^3 r (\rho(r), \nabla \rho(r))$$

(2-15)

Several GGA functionals have been implemented and amongst the most popular ones are (Becke 1986; Perdew 1986a; Perdew & Yue 1986; Perdew et al. 1996; Perdew 1986b; Lee et al. 1988; Becke 1988):

- Perdew-Wang 86 (PW86)
- Becke-Perdew (BP)
- Lee-Yang-Parr (LYP)
- Perdew-Wang 91 (PW91)
- Perdew-Burk-Enzerhof (PBE)
- Revised Perdew-Burke-Enzerhof (RPBE)

Many of these functionals include experimental parameters in order to obtain more accurate results for particular systems, e.g. solids. However, contrary to the majority of the functionals, PW91 is entirely ab-initio as it was built exclusively from LDA data. In the investigations presented in this thesis the PBE has been the functional employed.

The implementation of GGA functionals increases the computational effort but allows the prediction of more accurate structural, spectroscopic and electronic properties than with the LDA functional.

### 2.4 The electronic structure in periodic solids

The approximations discussed above aim to simplify the solution of the Schrödinger equation. However, further approximations can be applied for crystalline solids by
taking advantage of their symmetry elements. In the context of solid state only the
primitive unit cell can be considered, which reduces considerably the number of atoms
and therefore of electrons which are treated with the plane-wave basis sets.

2.4.1 Bloch’s theorem

An ideal solid is built by repeating periodically its unit cell. The Bloch’s theorem
(Bloch 1929) considers this translational symmetry to solve the one-electron
wavefunction in the unit cell instead of the entire periodic structure. The one-electron
wavefunctions determined for the unit cell are expanded to obtain the one-electron
wave functions for the entire periodic structure. The wavefunction of an electron in a
crystal is represented by a periodic part \( f_{i,k}(r) \) and a plane-wave like part \( e^{ikr} \):

\[
\psi_{i,k}(r) = f_{i,k}(r)e^{ikr}
\]  \hspace{1cm} (2-16)

As \( f_{i,k}(r) \) shares the same periodic character of the crystal, this function produces the
same result as \( f_{i,k}(r+T) \) when \( T \) is a translational vector with the crystal periodicity.
The periodic function \( f_{i,k}(r) \) is expanded as Fourier series in the reciprocal lattice:

\[
f_{i,k}(r) = \sum_{G} c_{i,k,G} e^{iGr}
\]  \hspace{1cm} (2-17)

Where the reciprocal lattice vector \( (G) \) is expressed as \( e^{iGT} = 1 \) and \( c \) corresponds to
the plane-wave expansion coefficients. From equations (2-16) and (2-17), we note that
the solutions for wavefunctions with index \( k + G \) are equal to the solutions for
wavefunctions with index \( k \). Thus, the solutions of these equations are similar to the
solutions for the \( k \)-points values of the primitive cell in the reciprocal space which is called the first Brillouin zone.

Different methods are available to define the \( k \)-points. Two of the most popular are the improved tetrahedron method (Blöchl et al. 1994) which divides the cell in the reciprocal space into tetrahedra, and the Monkhorst and Pack method (Monkhorst & Pack 1976) where the Brillouin zone is sampled in an equally-spaced mesh.

### 2.4.2 Plane wave expansion of the wavefunctions

Like every periodic function, Bloch functions can be expressed as a linear combination of plane waves. Thus, by substituting the expression of the periodic function from equation (2-17) in equation (2-16) allows the expansion of the wavefunction:

\[
\psi_{i,k}(r) = \sum_G c_{i,k+G} e^{i(k+G) \cdot r}
\]  

(2-18)

From equation (2-18) we note that the wavefunction \( \psi_{i,k}(r) \) is a function of the plane wave coefficients \( c_{i,k+G} \) meaning that solving the Kohn-Sham equations amounts to determine the set of \( c_{i,k+G} \) for which the energy is minimised.

To solve equation (2-18), an infinite plane-wave basis set is needed, which is computationally very expensive. Thus, the set of \( c_{i,k+G} \) for which the kinetic energy is high are ignored. \( c_{i,k+G} \) approaches to zero for plane-waves corresponding to high kinetic energy. Therefore, we only consider the plane-waves with a kinetic energy lower than certain cut-off: \( \frac{\hbar^2}{2m} |k + G|^2 < E_{\text{cutoff}} \) which reduces the search of the \( c_{i,k+G} \)
coefficients. Although the use of a finite basis set by specifying the kinetic energy cut-off simplifies considerably the problem, we still have to determine a significant number of plane-waves for both valence and core electrons. Pseudopotentials are a further simplification to reduce computational demand as calculations only treat explicitly the valence electrons.

2.5 Pseudopotentials

It is well known that the core electrons have a negligible influence on the chemical bonds. We can therefore apply the pseudopotential approximation which considers the core electrons of the system frozen. Thus, the valence electrons are considered moving in the external potential generated by the frozen core electrons, allowing to reduce the number of plane-waves required to solve the equation (2-18). The real wavefunctions, oscillating in the core region, are replaced by pseudo-wavefunctions containing zero nodes in the core region. The pseudo-wavefunctions behave identically to the true wavefunctions beyond certain distance from the atomic centre (see Figure 2-1).
Figure 2-1. Schematic illustration of all-electron (solid lines) and pseudoelectron (dashed lines) potentials and their corresponding wave functions. The radius at which all-electron and pseudoelectron values match is \( r_c \). Reproduced from (Payne et al. 1992).

Popular pseudopotentials are used in computational chemistry such as the ultrasoft pseudopotentials (US) (Vanderbilt 1990), the non-conserving pseudopotentials (NCPP) (P. E. Blöchl 1994) and the projected augmented wave pseudopotentials (PAW) (P. E. Blöchl 1994; Kresse & Joubert 1999) which is the one adopted in this investigation.

Unlike other pseudopotentials, the core electrons in the PAW model are characterised by a frozen nodal structure while the valence electrons are described by an all-electron wave-function. NCPP requires many planewaves for some elements, whereas one of the disadvantages of both NCPP and USPP is the non-negligible overlap between the valence- and core-electron density, which overlap is removed in the PAW method. Using the PAW pseudopotentials in solid state chemistry provides a faster
convergence of the pseudo-wavefunction than NCPP and USPP. Finally, NCPP requires larger plane-wave basis sets than PAW for transition metals such as Ni, which is one of the elements considered in this study, whereas USPP is less reliable than the PAW method for magnetic systems such as Ni (Kresse & Joubert 1999).

### 2.6 Dispersion interaction correction methods

So far, we have shown all the necessary approximations required in solid state chemistry to solve the Schrodinger equation. However, one of the drawbacks of the DFT approximation discussed so far is the failure to describe the long-range dispersion interactions, which are important in polarisable atoms, i.e. anions and atoms with large volumes. As we are describing the adsorption of molecules on zirconia surfaces, it is important to include the dispersion interactions in our calculations. Because of the local character of the DFT functionals, this method cannot correlate the electronic movement of isolated atoms (Ruzsinszky et al. 2005). A solution to this limitation is to add a correction $E_{vdW}$ to the pure Kohn-Sham DFT energy ($E_{KS-DFT}$) (equation (2-19)):

$$E_{DFT-vdW} = E_{KS-DFT} + E_{vdW}$$

A popular approximation to evaluate the correction term $E_{vdW}$, and the one used in this investigation, is the D2 method of Grimme (Grimme 2006) providing better structural and mechanical energies in comparison with pure DFT functionals (Bučko
et al. 2010). This method has the advantage of being not computationally expensive (Bučko et al. 2010). The D2 method evaluates the $E_{vdW}$ term as follows:

$$E_{vdW} = -\frac{s_6}{2} \sum_{A=1}^{M} \sum_{B=1}^{M} \sum_{L} \frac{C_{6AB}}{R_{AB,L}^6} f_{d,6}(R_{AB,L})$$

(2-20)

where $M$ is the number of atoms considered in the system, $C_{6AB}$ is the dispersion coefficient for the atom pair $AB$, $R_{AB,L}$ corresponds to the distance between atom $A$ placed in the reference cell and atom $B$ in the translation of the unit cell $L$. $s_6$ is a global scaling parameter specific for each DFT functional. $f_{d,6}$ is a Fermi-type damping function added to avoid double counting of the short-range interactions, which is expressed as follows:

$$f_{d,6}(R_{AB,L}) = \frac{1}{1 + e^{-d(R_{AB,L} - R_{vdW-AB})}}$$

(2-21)

where $d$ is the damping parameter and $R_{vdW-AB}$ is the sum of the atomic van der Waals radii of the atoms $A$ and $B$.

The geometric mean of the atomic $C_{6A}$ and $C_{6B}$ parameters is used to define the dispersion coefficient $C_{6AB}$.

Other dispersion correction methods include the D3 method of Grimme et al. (Grimme, Antony, et al. 2010), the D3 (zero) damping method (Grimme, Ehrlich, et al. 2010), the Tkatchenko- Scheffler (TS) method (Tkatchenko & Scheffler 2009), the TS+SCS self-consistent screening method (Tkatchenko et al. 2012). Nevertheless, the expressions for the D3 and D3(zero) methods are more complex, compared to the
parent D2 method. As to the TS and TS+SCS methods, both fail to describe properly strong ionic systems (Bučko et al. 2013).

2.7 Geometry optimization

To solve the DFT equations, two minimizations are required: one to find the electronic ground state and a second one to determine the position of the nuclei that minimizes the energy.

2.7.1 Optimisation of ionic positions: the conjugate gradients method

The conjugate gradients (CG) method is a popular algorithm employed to locate the minimum of a function with several variables (Gill et al. 1981). This method aims to calculate the energy function \( E(R) \) and its gradient with respect to the nuclei coordinates \( R \), which is equivalent to solve the Hellmann-Feynman theorem (Hellmann 1937; Feynman 1939) for a given system.

The CG method is based on the steepest descent (SD) algorithm where atoms are moved towards the direction of the force \( F \) (see Figure 2-2).

![Steepest descent vs conjugate gradients](image)

**Figure 2-2.** Steepest descent (a) vs conjugate gradients (b)
In the SD method, $E(R)$ is first determined along a line at regular intervals between two points. Thus, starting from an initial position $R_1$, the next position is evaluated as:

$$R_2 = R_1 + b_1 F(R_1)$$  \hspace{1cm} (2-22)

where $b_1$ is determined to satisfy $F(R_2) \cdot F(R_1) = 0$.

The new gradient $F(R_2)$ is orthogonal to the previous line and the process is repeated from the new point to the direction of $F(R_2)$ until the minimum is found. The SD method goes always downhill and it avoids saddle points. However, it searches in a ‘zigzag’ pattern as the direction of the $i^{th}+1$ step has to be perpendicular to the direction of the $i^{th}$ step. The method becomes slow in the vicinities of the minimum where it is computationally expensive, requiring a large number of steps before locating the minimum.

The CG method differs from the SD method after the initial step. The ‘zigzag’ pattern to locate the minimum is avoided in the CG method as the successive displacements can take any direction and the expression of the algorithm is as follow:

$$R_{m+1} = R_m + b_m S_m$$  \hspace{1cm} (2-23)

The information from the gradient and the search direction from the previous step are enclosed in the search vector $S_m$ (see equation (2-24)):

$$S_m = F(R_m) + \gamma_m S_{m-1}$$  \hspace{1cm} (2-24)

Where the scalar coefficient $\gamma_m$ is equal to zero for $m = 1$. Fletcher and Reeves (Fletcher & Reeves 1964) have defined the latter scalar parameter as follow:
\[
\gamma_m = \frac{F(R_m) \cdot F(R_{m+1})}{F(R_{m-1}) \cdot F(R_{m-2})}
\] (2-25)

Compared to the SD method, the CG method has the advantage to use fewer number of steps for searching the minimum of the energy function. The search directions are optimally independent from each other, i.e. conjugate. Thus, the minimum of a quadratic function of M variables can be found in M iterations (Figure 2-2 b)).

The CG method is implemented in the VASP software and it employs a line minimization following three steps: i) a trial step into search direction is performed followed by the evaluation of the energies and the forces. ii) A cubic (or quadratic) interpolation of the total energy is carried out and the approximate minimum of the total energy is defined. This is followed by the evaluation of the corrector step, which are the positions corresponding to the anticipated minimum. iii) After evaluation of the corrector step, the forces and energy are recalculated. If there is still a significant component parallel to the previous search direction, a further corrector step is performed until convergence is achieved.

2.7.2 Relaxation of cell parameters: Pulay stress and equation of state method

Francis and Payne (Francis & Payne 1990) reported that the “Pulay stress” may be generated if cell parameters are optimised in addition to the atoms’ positions. The number of plane waves in the basis set is determined by the cut-off energy and the size of the reciprocal lattice cell. Thus, for a given energy cut-off, the optimisation of the cell parameters will change the volume of the reciprocal lattice cell and the number of
the plane waves in the basis set. The consequence of this error is similar to a positive pressure applied to the cell which reduces its volume.

A solution to the Pulay stress error is to fix a cut-off energy approximately 1.3 times higher than the value required for energy convergence. However, a higher energy cut-off slows down the calculations, as more plane waves are considered. Another solution to avoid the Pulay stress without increasing the energy cut-off value is to relax internal coordinates for a series of fixed volume cells. Thus, the Pulay stress is avoided as the volume remains constant during the calculations. In this thesis, we have avoided the problem of the Pulay stress by evaluating the cell parameters by using single point calculations for different values whilst keeping the internal coordinates fixed. Thus, the volume remains constant during the single point calculations and therefore the Pulay stress is nil. The energy can be expressed as a function of the volume and by fitting the calculated energy to a cubic equation of state, it is possible to calculate the equilibrium volume of the cell.

2.7.3 Transition states

So far, this chapter has been focused on the techniques used to determine the minimum of the energy function. Note that an energy function can have several local minima and those minima are linked by transition states along the reaction coordinates (see Figure 2-3) (e.g. for chemical reactions, adsorptions or diffusion processes).
Transition states are the saddle points with the lowest energy between two minima and they represent the high energy state for atomic rearrangements. The activation energy, the most important parameter characterising a transition state, corresponds to the difference between the initial minimum state and the saddle point (Figure 2-3).

Several techniques have been developed for searching the reaction coordinates and the saddle point (Henkelman et al. 2002). In this thesis, two popular methods have been considered: the climbing image nudged elastic band (cNEB) method (Henkelman et al. 2000; Sheppard et al. 2008) and the improved dimer method (IDM) (Heyden et al. 2005). The cNEB is based on the nudged elastic band (NEB) (Mills et al. 1995;
Sheppard et al. 2008) where the saddle point is examined between the initial and final states. The aim of this method is to determine intermediate images, along the reaction coordinate (band), between the reactants and the products. During the optimization, the adjacent images are kept equidistant by adding spring forces, which allows the continuity of the band like an elastic band. The geometry of the intermediate states is optimized until the forces acting on their atoms reach certain defined threshold.

The cNEB uses fewer images than the NEB while providing a more accurate final geometry of the saddle point. In the cNEB algorithm, the spring constraint is not applied to the intermediate having the highest energy. To maximize the energy of this intermediate along the band and minimize it in all other directions, the force of the intermediate is inverted along the tangent. The optimized image of this intermediate corresponds to the saddle point.

The IDM is also implemented in VASP and is an improvement of the original dimer method (Henkelman & Jónsson 1999). This algorithm requires only one initial state and the dimer axis related with the unstable mode which can be estimated from a vibrational calculation discussed in the next section.

2.8 Characterization of the optimised geometries

Optimised geometries are points on the potential energy surface where the gradients of each vibrational mode are equal to zero. These states can be a local or global minimum, or a saddle point on the hypersurface. Optimised geometries are particular points hence the interest of this section on the methodologies used for characterizing
their properties, such as: vibrational frequencies, density of states, atomic charges and atomic spin densities.

### 2.8.1 Vibrational frequencies

Evaluating the vibrational modes of a system is useful for two reasons: i) to discern whether the optimized geometry is a minimum (local or global) or a transition state (TS) and ii) to simulate the infrared (IR) or Raman spectra, which can be compared with experimental data.

The vibrational frequencies are obtained from the second derivative of the potential energy. Second derivatives are positive for the minimum states, meaning that all the vibrational frequencies are real. For a saddle point, all the second derivatives of the potential energy are positive except the imaginary one, associated with the unstable mode of the saddle point (Komornicki & McIver 1976).

The VASP software follows a numerical method to evaluate the vibrational frequencies, where each atom is displaced in the direction of each Cartesian coordinate. The second derivatives of the potential energy with respect to these displacements leads to the Hessian matrix (see equation (2-26)). The eigenvalues and eigenvectors of the Hessian matrix correspond to the vibrational frequencies and vibrational modes, respectively, of the system.
In this thesis, we consider that the vibrational frequencies of the adsorbate and the phonons of the surface are decoupled. This simplifies the calculations for adsorbate-surface systems as we neglect the phonons contribution.

### 2.8.2 Density of states

An important aim of the computational chemistry is to understand the origin of the chemical bonds. The density of states (DOS) facilitates the characterization of chemical bonds in the context of solid state. As a periodic solid has a large number of atoms, the discrete energy levels related to the different atoms are similar which results in the formation of continuous bands. These energy bands can be evaluated from the DOS, which corresponds to the number of states available to electrons per unit cell at a specified energy. There are two kinds of bands: the valence band which is below the Fermi level ($E_F$) and correspond to the occupied states, and the conduction band which is above the Fermi level and corresponds to the unoccupied states. The DOS can be projected onto atomic orbitals which gives the projected DOS (PDOS). The PDOS are useful to investigate the atomic states involved in the formation of chemical bonds. The intensity and position of the PDOS bands provide information on the different electronic interactions occurring in the system such as a charge...
transfer, ionic or covalent interactions. For spin polarised calculations, the DOS give also information about the up (α) and down (β) electronic spin channels.

2.8.3 Localisation of the electrons

2.8.3.1 Bader charge analysis

An approach to characterize the chemical bonds within a system is the evaluation of charge transfers from atomic charges. Bader et al. (Bader et al. 1987) proposed the theory of atoms in molecules (AIM) based on the Lewis model and the Valence Shell Electron Pair Repulsion (VSEPR) for the topological analysis of the electronic density (Bader et al. 1988; Bader 1990; Bader 1994). In this method, the electron density is divided into subsystems separated by zero-flux surfaces of electronic density. The Bader basin corresponds to the volume enclosed by this surface where the atomic charge is evaluated. Although the Bader partition scheme is not sensitive to the basis set used, it underestimates ionic charges because of the electron delocalization in DFT. However, this method allows to define general trends in term of charge transfer within the system.

2.8.3.2 Electronic density

The electronic density is a powerful tool to understand the electronic interactions occurring within the system. It is possible to plot an electronic density difference map where density of charge gain and charge depletion are shown after a covalent bond formation.
2.8.3.3 Electron localization function

Another approach to characterize the different chemical interactions in the system is the determination of the electron localization function (ELF) (Becke & Edgecombe 1990; Silvi & Savin 1994). Silvi et al. (Silvi & Savin 1994) explained that the ELF evaluates the influence of the Pauli repulsion on the electrons behaviour. Thus, it allows to determine the regions where we have paired electrons.

2.9 Solid models

2.9.1 Bulk models

We can represent a perfect periodic solid by the infinite 3-dimensional repetition of its unit cell. The primitive unit cell is the smallest unit of volume where all the necessary information, such as the structure and the symmetry, is contained in order to generate, by translation, the macroscopic structure. However, in some cases, research is carried out using the conventional unit cell which has higher symmetry. For instance, the crystal structure of nickel bulk is Fm3m (face-cantered) with the atoms located at the cube vertex and on the face centre of the conventional unit cell. This cubic face-centred fragment is therefore the unit cell. Thus, the Schrödinger equation is solved only for this unit cell by taking advantage of the Bloch’s theorem—section 2.4.1. To model the interaction of this system or its surfaces with perturbing element such as adsorbate or defects, a supercell (see following section 2.9.2) is required to avoid interaction between the images of the perturbing elements.
2.9.2 Surface models

The surface model is generated by cleaving the bulk along crystallographic planes. The Miller indices correspond to three integers written as \((h \ k \ l)\) which define a family of lattice planes. Each index defines a plan orthogonal to an \((h, k, l)\) direction in the basis of the reciprocal lattice vectors.

The generated surface is the place where the perturbing elements such as liquids or molecules from the gas phase are in contact with the crystal. There are two general approaches to model surfaces: the cluster model and the periodic slab model. In the cluster model the surface is built up by forming a small isolated cluster of atoms. In the periodic slab model (used in this thesis) a supercell is built containing several atomic layers (the slab) and a vacuum (Figure 2-4).

![Figure 2-4. Schematic representation of the periodic slab model.](image-url)
The size of the vacuum has to be large enough to avoid unwanted interactions between the slab and its images. The optimal vacuum size is determined by finding the value that converges the energy of the system. The slab thickness also has to be large enough to avoid interaction between the surfaces from both sides of the slab. The best slab thickness is evaluated by calculating the surface energy as a function of the atomic layers in the slab, until the unrelaxed surface energy ($\gamma_F$) reaches a constant value (see equation (2-27)).

$$\gamma_F = \frac{E_F - nE_B}{2 \cdot A}$$

(2-27)

$E_F$ is the total energy of the surface slab with all atomic layers fixed), $n$ is the factor of proportionality that makes the number of atoms in the bulk equal to the number of atoms in the surface slab, $E_B$ is the bulk energy, and $A$ is the surface area of one side of the slab (see Figure 2-4).

Once the slab and vacuum size that converge the energy have been found, the last step is to find the number of atomic layers to relax while keeping the rest fixed in their bulk positions. For this, the relaxed surface energy is calculated with respect to the number of relaxed atomic layers until the relaxed surface energy ($\gamma_R$) converges (see equation (2-28))

$$\gamma_R = \frac{E_R - nE_B}{A} - \frac{E_F - nE_B}{2 \cdot A} = \frac{E_R - nE_B}{A} - \gamma_F$$

(2-28)

$E_R$ is the total energy of relaxed surface slab. Experimentally, the surface energy is the energy required to cut the bulk crystal and expose the surface. Thus, the values of $\gamma_R$ found from DFT calculations can be compared with experimental studies.
Figure 2-5 summarises all the steps discussed to create the slab model which will be the basis for the calculations of this thesis.

**Figure 2-5.** Schematic representation of the methodology used to generate the zirconia slab model.
Chapter 3

Single nickel adsorption on ZrO$_2$ and YSZ surfaces

Abstract

In this chapter we have investigated both pristine and doped ZrO$_2$ surfaces using spin polarized density functional theory (DFT) and also considering long-range dispersion forces. We have systematically studied Ni deposition on the bare ZrO$_2$(111) surface and on surfaces with two concentrations of Y, all at both high and low oxygen chemical potential. Among the several independent sites explored, the Ni adsorption preference is as follow: YSZ(111) without oxygen vacancy > YSZ(111) with oxygen vacancy > stoichiometric ZrO$_2$(111). For each surface, the adsorption site is similar: over the top oxygen. The evaluation of the geometric and electronic structure shows a mixing of Ni orbitals with surface atom orbitals. We have also investigated the influence of the yttrium atom on the Ni adsorption by considering up to 52 different configurations, which showed that Ni tends to adsorb away from the yttrium atom for any YSZ(111) surface, leading to a mixed electronic structure with enhanced charge transfer.
3.1 Introduction

As was stated in the introduction of this thesis, several barriers must be overcome to make SOFC commercially competitive with traditional combustion power plants. For instance, the efficiency must be improved, the catalysts need to be highly tolerant to fuel impurities and the high working temperature (approximately 500-900 °C) (Jacobson 2010; Sun et al. 2009) should be lowered. Thus, care is needed to choose suitable components for SOFC. In chapter 1 we have seen that a suitable anode material is Ni/YSZ cermet as it has a high catalytic activity, mechanical/chemical stability and compatibility with the electrolyte. The performance of the Ni/YSZ cermet depends on its microstructure as well as the Ni distribution in the cermet (Kim et al. 2006). Thus, in order to improve the performance of the anode, it is crucial to understand the Ni/YSZ interaction.

Cubic Zirconia (c-ZrO$_2$) is one of the three polymorphs of pure ZrO$_2$, and stable at atmospheric pressure at temperatures between 2650 K and 2950 K (polymorph melting point). Between 1400 K and 2650 K ZrO$_2$ is tetragonal and below 1400 K the stable phase is monoclinic zirconia (Bogicevic et al. 2001; Aldebert & Traverse 1983). However, when the cubic phase is doped with a cation of lower valence, like Y, the c-ZrO$_2$ phase is stabilized at lower temperatures (below 800 K) and therefore present in the SOFC, in addition to being used in many other catalytic applications (Stefanovich et al. 1994; Guo 2000; Yucai 2005; Wang et al. 2005; Ramaswamy et al. 2004; Dongare et al. 2004; Mercera et al. 1991).
Oxygen vacancies play an important role in the process of the SOFC since the conductivity of the anions (O$^{2-}$) is achieved through these vacancies (Eichler 2001). Oxygen vacancies are created when the cubic zirconia is doped with Y$^{3+}$, and the number of oxygen vacancies thus increases with the concentration of Y, leading to increased oxygen diffusion through the YSZ cermet. However, the anion conductivity reaches a maximum at a dopant concentration of about 8 %, whereas at higher dopant concentrations the anion conductivity decreases (Badwal 1992). The reason for this behaviour is still unclear although theoretical investigations have tried to explain this non-monotonic behaviour. For example, a recent study using first principles calculations (Pietrucci et al. 2008) has shown that vacancy-vacancy interactions could affect the diffusion of oxygen in the YSZ cermet.

Several ab-initio studies have modelled the Ni/YSZ interface (Shishkin & Ziegler 2009; Anderson & Vayner 2006; Cucinotta et al. 2011). However, a systematic study of the electronic structure of a Ni atom over the YSZ surface, considering most of the adsorption sites and configurations, and taking into account different positions of the Y atoms and oxygen vacancies is still lacking. We have therefore analysed the electronic structure of YSZ with different concentrations of yttrium to unravel vacancy-Ni interactions. We have considered four configurations of the Y-stabilized ZrO$_2$(111) surface, showing the effect of the Y atom on the adsorption of Ni.
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3.2 Model and computational details

The calculations were performed using the Vienna Ab-initio Simulation Package (VASP) (Kresse & Furthmüller 1996b; Kresse & Furthmüller 1996a; Kresse & Hafner 1993; Kresse & Hafner 1994), which solves the Kohn-Sham equations of the density functional theory (DFT) (Hohenberg & Kohn 1964) in a periodic system. The method employed here is the generalized gradient approximation (GGA) (Perdew et al. 1996) with the Perdew-Burke-Ernzerhof (PBE) density functional. To describe the long-range dispersion interactions, we have used the semiempirical method of Grimme (Grimme 2006). The core electrons, up to and including the 4 p levels of Zr, the 1 s of O, the 3 p of Ni and the 3 d of Y were frozen and their interaction with the valence electrons was described by the projected augmented wave method (PAW) (P E Blöchl 1994). We tested inclusion in the valence bands of the p-levels on Zr but this resulted in negligible changes in the electronic structure and system energies. All the calculations were spin polarized. The number of plane-waves in VASP depends on the cutoff energy which was fixed at 500 eV in our calculations. To optimize the geometry of the structure, we have used the conjugate gradient technique and the ionic relaxation loop was stopped when the forces acting on the atoms were less than 0.01 eV/Å. To sample the reciprocal space for the ZrO\textsubscript{2} bulk calculations a 9x9x9 mesh of k-points was adopted, while for the slab calculations a 7x7x1 mesh of k-points was used.

Cubic zirconia (c-ZrO\textsubscript{2}) has the fluorite crystal structure: a face centred cubic (fcc) unit cell (space group Fm\textsubscript{3}m) shown in Figure 1-6. The Zr atoms are arranged in the unit cell to form the fcc cube, each coordinated to 8 oxygen. The position of the O atoms is on the diagonals of the cube.
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Figure 3-1. Crystal structure of cubic zirconia (c-ZrO$_2$). Colour key: red and grey spheres correspond to oxygen and zirconium atoms, respectively.

To generate the ZrO$_2$(111) surface from the bulk, the METADISE code (Watson et al. 1996) was used which takes into account the periodicity in the plane direction and the atomic charges. Stacking of the atomic layers resulting in a zero dipole moment perpendicular to the surface plane was obtained using this code, although we could also have obtained it by using the electron counting method (Santos-Carballal et al. 2014). We explored the different terminations of the surface and found that the O-terminated ZrO$_2$(111) is the most stable, in agreement with the benchmark (Graucrespo et al. 2007). We have used a supercell model where the surface is represented by a slab of material with two infinite surfaces at either side of the slab and vacuum between the slab and the next cell. For a vacuum size of 15 Å and a slab thickness of 9 atomic layers (three O-Zr-O trilayers) in the z-direction acceptable convergence of the surface properties was reached. Each atomic layer contains four atoms resulting in a 36 atom slab with surface areas of $44.96 \, \text{Å}^2$. During optimization, the five top atomic layers were relaxed while the four atomic layers at the bottom were kept fixed, thereby simulating the bulk. The thickness of the slab and the number of relaxed layers form
a good model, where atoms in the centre of the slab behave as in the bulk without undergoing significant relaxation. Finally, since the conductivity of $O^{2-}$ in YSZ reaches its maximum for a concentration of dopants around 8%, we built a YSZ surface containing this amount of dopant (and lower) and we placed Y in several non-equivalent positions.

In line with a previous study (Beltrán et al. 2003), we initially positioned the Ni atom at 2 Å above an initial adsorption site and relaxed, for each site, the Ni atom and the five top layers of the slab, as described in the computational methods section. We determined the binding energy ($E_B$) for each site as the difference between the energy of the slab with the Ni atom adsorbed ($E_{ZrO_2/Ni}$) and the sum of the energies of the clean oxide surface ($E_{ZrO_2}$) and Ni metal ($E_{Ni}$), as in equation (3-1).

$$E_B = E_{ZrO_2/Ni} - (E_{ZrO_2} + E_{Ni})$$

$E_{Ni}$ is the energy per Ni atom calculated from the Ni bulk. A positive binding energy indicates that Ni atoms prefer to remain aggregated in the metal phase rather than wet the surface, leading to separated phases: Ni$_{(s)}$ and ZrO$_2(s)$. A negative binding energy suggests that Ni atoms are more likely to be spread over the surface rather than aggregated.

### 3.3 Results and discussion

We first determined the cell parameter of our cubic bulk ZrO$_2$ structure, since the surface slab is generated from the bulk material. Our optimized c-ZrO$_2$ cell parameter is 5.095 Å, in good agreement with experimental results and other first principles
quantum mechanical calculations (Stapper et al. 1999; Xia et al. 2009). The O-terminated ZrO$_2$(111) surface was geometry optimized giving a calculated surface energy of 1.20 J$\cdot$m$^2$ in agreement with previous publications (Grau-crespo et al. 2007; Grau-Crespo et al. 2009; Chauke et al. 2010; Grau-Crespo, R., Catlow, C. R. A., de Leeuw, N. H., Neyman, K., Illas 2007). We have also calculated the surface energies of two other low index surfaces, the (110) and (100), and compared these with previous studies (Table 3-1), which found the same order of surface stabilities as in our study: c-ZrO$_2$(111)>c-ZrO$_2$(110)>c-ZrO$_2$(100). This agreement with other methods gives us confidence that the methodology used here accurately describes the material’s structural properties.

Table 3-1. Calculated surface energies (J/m$^2$) of c-ZrO$_2$(111), c-ZrO$_2$(110) and c-ZrO$_2$(100) and comparison with previous studies.

<table>
<thead>
<tr>
<th></th>
<th>(111) unrelaxed</th>
<th>(111) relaxed</th>
<th>(110) unrelaxed</th>
<th>(110) relaxed</th>
<th>(100) unrelaxed</th>
<th>(100) relaxed</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>1.26</td>
<td>1.20</td>
<td>2.31</td>
<td>1.70</td>
<td>4.33</td>
<td>2.67</td>
</tr>
<tr>
<td>ref.(Christensen &amp; Carter 1998) (DFT-LDA$^a$)</td>
<td>1.19</td>
<td>--</td>
<td>2.29</td>
<td>--</td>
<td>3.06</td>
<td>--</td>
</tr>
<tr>
<td>ref.(Gennard et al. 1999) (HF$^b$)</td>
<td>1.51</td>
<td>1.49</td>
<td>3.04</td>
<td>2.41</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ref.(Balducci et al. 1998) (IP$^c$)</td>
<td>--</td>
<td>1.19</td>
<td>--</td>
<td>2.10</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ref.(Xia et al. 2009) (IP$^c$)</td>
<td>1.45</td>
<td>1.21</td>
<td>3.64</td>
<td>2.15</td>
<td>10.06</td>
<td>2.70</td>
</tr>
<tr>
<td>ref.(Grau-crespo et al. 2007) (DFT-GGA$^d$)</td>
<td>--</td>
<td>1.08</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$ DFT-LDA = Density Functional Theory – Local Density Approximation
$^b$ HF = Hartree-Fock
$^c$ IP = Interatomic Potential
$^d$ DFT-GGA= Density Functional Theory – Generalized Gradient Approximation
Figure 3-2 shows side and top views of the (111) surface where Zr, top O and lower O are labelled. We calculated a ZrO$_2$(111) band gap of 3.40 eV (Figure 3-3 (a)), i.e. slightly larger than in the c-ZrO$_2$ bulk (~3.14 eV) (Shishkin & Ziegler 2008), but lower than the experimentally measured bulk values (5-6 eV) (French et al. 1994; Sayan et al. 2004), in common with most computational studies (Shishkin & Ziegler 2008; Alfredsson & Richard A. Catlow 2001).

3.3.1 Ni/ZrO$_2$(111) interface

For our study of the deposition of a Ni atom on the surface and the resulting geometry and electronic structure of the system, we considered seven different Ni adsorption sites on the O-terminated ZrO$_2$(111): the Zr atom, the topmost oxygen O$_u$ (up) (located in the top oxygen layer), O$_d$ (down) (located in the lower oxygen layer of the uppermost ZrO$_2$ trilayer), the position between each pair of sites (O$_u$-Zr, O$_u$-O$_d$ and O$_d$-Zr) and finally above the centre of the O$_u$-O$_d$-Zr “triangle”.

![Diagram](image.png)

Figure 3-2. Side and top views of the O-terminated ZrO$_2$(111) surface. Colour key: red and grey spheres represent oxygen and zirconium atoms, respectively.
The binding energies for the optimized structures of Ni deposited on the surface ranged from 2.42 eV on the O₆-O₆-Zr to 3.76 eV for the Zr initial positions, which relaxed to a final position O₆’ (slightly off from the perpendicular), which has the lowest binding energy and is therefore the most probable adsorption site for the Ni atom on the ZrO₂(111) surface, although still very positive and thus energetically unfavourable.

We analysed the electronic structure of the Ni/ZrO₂(111) for the most stable adsorption site (O₆’), and identified charge transfer between the Ni atom and the surface using Bader analysis with the Henkelman implementation (Bader 1991). Table 3-2 shows the Bader charges of the bare and Ni(O₆’)/ZrO₂(111) surfaces. The negative charge of the O₆ atom decreases from -1.2 to -1.1 e upon Ni adsorption, while it increases for Zr (from 2.3 e to 2.1 e upon Ni adsorption) showing electronic rearrangement. Ni has a Bader charge of 0.3 e upon adsorption, showing modest oxidation of metallic Ni which transfers electrons to the surface (see Table 3-2).
**Table 3-2.** Calculated binding energies, distances and charges for the 5 surfaces. The charges given here are the average of the closest Oₜ, Oₜ and Zr atom to Ni adsorption site and for adsorbed Ni. The distances showed here are between Ni and the closest Oₜ, Oₜ and Zr atom.

<table>
<thead>
<tr>
<th>binding energy (eV)</th>
<th>ZrO₂(111)</th>
<th>Zr₁₁Y₂O₃(111)</th>
<th>Zr₁₁Y₂O₃(111)</th>
<th>Zr₁₀Y₂O₃(111)</th>
<th>VAC-Zr₁₀Y₂O₃(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2.42</td>
<td>0.05</td>
<td>0.02</td>
<td>-1.65</td>
<td>2.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>distances (Å)</th>
<th>ZrO₂(111)</th>
<th>Zr₁₁Y₂O₃(111)</th>
<th>Zr₁₁Y₂O₃(111)</th>
<th>Zr₁₀Y₂O₃(111)</th>
<th>VAC-Zr₁₀Y₂O₃(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Oₜ</td>
<td>1.900</td>
<td>1.867</td>
<td>1.851</td>
<td>1.904</td>
<td>1.958</td>
</tr>
<tr>
<td>Ni-Oₜ</td>
<td>2.614</td>
<td>2.798</td>
<td>2.855</td>
<td>2.796</td>
<td>--</td>
</tr>
<tr>
<td>Ni-Zr</td>
<td>2.355</td>
<td>2.525</td>
<td>2.545</td>
<td>2.947</td>
<td>2.487</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>bader Charge (e)</th>
<th>ZrO₂(111)</th>
<th>Zr₁₁Y₂O₃(111)</th>
<th>Zr₁₁Y₂O₃(111)</th>
<th>Zr₁₀Y₂O₃(111)</th>
<th>VAC-Zr₁₀Y₂O₃(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare.</td>
<td>-1.2</td>
<td>-1.1</td>
<td>-1.2</td>
<td>-1.2</td>
<td>-1.2</td>
</tr>
<tr>
<td>Ni Ads.</td>
<td>-1.2</td>
<td>-1.2</td>
<td>-1.2</td>
<td>-1.2</td>
<td>-1.2</td>
</tr>
<tr>
<td>bare.</td>
<td>-1.1</td>
<td>-1.2</td>
<td>-1.2</td>
<td>-1.2</td>
<td>-1.2</td>
</tr>
<tr>
<td>Ni Ads.</td>
<td>-1.1</td>
<td>-1.8</td>
<td>-1.2</td>
<td>-1.2</td>
<td>--</td>
</tr>
<tr>
<td>bare.</td>
<td>2.3</td>
<td>2.1</td>
<td>2.3</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Ni Ads.</td>
<td>2.3</td>
<td>2.2</td>
<td>2.3</td>
<td>2.3</td>
<td>2.1</td>
</tr>
</tbody>
</table>

We also plotted the density of states (DOS) and its projection (PDOS) on Ni, Zr and Oₜ, in Figure 3-3.
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Figure 3-3. (a) and (b) show the electronic density of states (DOS) of ZrO$_2$(111) and Ni/ZrO$_2$(111), respectively. (c) and (d) show the composition of the valence band of the projected DOS of ZrO$_2$(111) and Ni/ZrO$_2$(111) respectively.

Upon deposition, the Ni d-orbitals are just below the Fermi energy: five sharp peaks appear just below the Fermi level (-1.33, -0.87, -0.56, -0.38 and -0.04 eV) (Figure 3-3 (b)) from the hybridization of Ni s- and d- orbitals. The double occupation of these orbitals agrees with the negligible charge transfer. Furthermore, we note that both α and β band spins are symmetrical, indicating no particular orientation of the spins.

Looking at the DOS plots of the atoms involved in the O$_u$-O$_d$-Zr site, before Ni adsorption (Figure 3-3 (c)), the PDOS of Zr does not contain localised bands below the Fermi level and the PDOS of O$_u$ and O$_d$ are spread along a wide range of energy.
However, upon Ni deposition, the five sharp bands below the Fermi level belong to O\textsubscript{u} 2p, O\textsubscript{d} 2p, Zr 4d, Ni 3d and Ni 4s orbitals (**Figure 3-3 (d)**) indicating interaction between those atoms. Similar observations were made by former studies for different metal adsorbates (Grau-crespo et al. 2007), showing s-d hybridization of the adatom orbitals and mixing of these orbitals with the ones belonging to the O\textsubscript{u} and Zr. Our investigation of Ni adsorbed on ZrO\textsubscript{2}(111) surface can be compared with the study made by Choi et al. (Choi et al. 2016), who have used scanning tunnelling microscopy (STM) to investigate the structures, cluster densities and growth mechanisms of Ag, Au, Pd, Ni, and Fe on an ultrathin ZrO\textsubscript{2} surface, grown by oxidation of Pt\textsubscript{3}Zr(0001) and Pd\textsubscript{3}Zr(0001). They have also complemented their experiment by DFT calculations to provide further insight. Their STM results indicated that the strength of the metal-oxide interaction follows the trend: Ag < Pd ~ Au < Ni ~ Fe. A clustering of Ag and Pd was observed at steps and domain boundaries of the ZrO\textsubscript{2}/Pt\textsubscript{3}Zr(0001) system, while Ni and Fe formed clusters of a few atoms on the oxide terrace. The authors’ cluster density analysis showed that the deposition of Ni (0.1 ML coverage) on ZrO\textsubscript{2}/Pt\textsubscript{3}Zr leads to an average cluster size of four atoms. At a coverage of 0.1 ML Ni on ZrO\textsubscript{2}/Pd\textsubscript{3}Zr the average number of atoms per cluster was found to be 1.6.

DFT calculations were carried out on the adsorption of the metal on both the monoclinic ZrO\textsubscript{2}(\bar{1}11) surface (a distorted version of the (111) surface of cubic ZrO\textsubscript{2}) and an ultrathin ZrO\textsubscript{2} surface. To model the ultrathin ZrO\textsubscript{2} surface, the authors considered a ZrO\textsubscript{2}(111) trilayer on top of a pure Pt (111) surface. On the monoclinic ZrO\textsubscript{2}(\bar{1}11) (m-ZrO\textsubscript{2}(\bar{1}11)) surface, by plotting the PDOS of Ni they showed that the Ni d states are located in the ZrO\textsubscript{2} band gap, similar to our investigation (**Figure 3-3**).
They also showed an interaction of Ni d states with both O and Zr surface atoms, which is comparable to our PDOS plot shown in Figure 3-3 (d). On the ultrathin ZrO$_2$ film a broadening of the d states was observed and a stronger interaction with the oxygen states of the valence band.

3.3.2 ZrO$_2$(111) stabilisation by Y

We next studied the effect of Y atoms on the interaction between Ni and the YSZ(111) surface. We doped the optimized ZrO$_2$(111) surface with one and two Y atoms, also varying the oxygen amount which allowed us to evaluate changes in the electronic structure under oxygen rich and poor conditions. To simulate the Y doped surfaces, without the oxygen vacancy, we do not need to define the initial charge of the material: in VASP software, the electrons will be attributed to the more electronegative species, according to their pseudopotentials, defining the charge of each species. The consequence of that is the appearance of an empty oxygen orbital above the Fermi energy. This, will be discussed later in this section.

3.3.2.1 Zr$_{11}$YO$_{24}$(111) surface

From the different potential substitutions of Zr by Y, we analysed two non-equivalent configurations. In the first one, we substituted a Zr belonging to the top O-Zr-O trilayer (Zr$_{11}$YO$_{24}$(111) - Figure 3-4 (a)); in the second configuration, we changed one Zr from the sub O-Zr-O trilayer (Zr$_{11}$YO$_{24}$(111) - Figure 3-4 (b)). Before adsorbing the Ni atom on these two surfaces, we carried out a geometry optimization for each configuration and analysed the effect of the Y atom on the clean ZrO$_2$(111) surface.
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Figure 3-4. (a) and (b) side view of the Zr$_{11}$Y$_{24}$O$_{24}$(111) and Zr$_{11}$Y$_{24}$O$_{24}$(111) surfaces, respectively. (c) top view of Zr$_{11}$Y$_{24}$O$_{24}$(111) showing the 19 non-equivalent initial adsorption sites for Ni atom. (d) top view of Zr$_{11}$Y$_{24}$O$_{24}$(111) showing the 20 non-equivalent initial adsorption sites for Ni atom. (e) and (f) most stable adsorption site for Ni on Zr$_{11}$Y$_{24}$O$_{24}$(111) and Zr$_{11}$Y$_{24}$O$_{24}$(111), respectively. Colour key: red, grey, cyan and blue spheres correspond to oxygen, Zr, Y and Ni atoms, respectively.

Comparing both Zr$_{11}$YO$_{24}$ surfaces, the energy difference per Y atom is negligible (0.02 eV) meaning that Y can, in principle, be located at the surface or in the subsurface.

Table 3-3 shows the variation of the distances between the different atomic layers upon Y substitution compared to the pristine ZrO$_2$(111) surface. We note that for both configurations, Zr$_{11}$Y$_{24}$O$_{24}$(111) and Zr$_{11}$Y$_{24}$O$_{24}$(111), the distances between the atomic layers are larger than the distances in the pristine ZrO$_2$(111) surface. This is not surprising since the ionic radius of Y is bigger than Zr (Eichler 2001). The
rumpling shows clearly that embedding Y modifies the surface locally which may be detectable by constant height STM.

**Table 3-3.** Main variation of the distance between the different atomic layers (in \%) upon Y substitution in the ZrO$_2$(111).

<table>
<thead>
<tr>
<th>layers</th>
<th>Zr$<em>{11}$Y$</em>{top}$O$_{24}$</th>
<th>Y$<em>{sub}$Zr$</em>{11}$O$_{24}$</th>
<th>Zr$<em>{10}$Y$</em>{2}$O$_{24}$</th>
<th>Y$<em>2$Y$</em>{sub}$Zr$<em>{10}$O$</em>{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>top - 2$^{nd}$</td>
<td>+5.7</td>
<td>+4.0</td>
<td>+8.7</td>
<td>+10.0</td>
</tr>
<tr>
<td>2$^{nd}$ - 3$^{rd}$</td>
<td>+2.9</td>
<td>+4.0</td>
<td>-1.8</td>
<td>+1.8</td>
</tr>
<tr>
<td>3$^{rd}$ - 4$^{th}$</td>
<td>+1.9</td>
<td>+0.1</td>
<td>+3.1</td>
<td>-4.6</td>
</tr>
<tr>
<td>4$^{th}$ - 5$^{th}$</td>
<td>-1.8</td>
<td>+8.8</td>
<td>+5.1</td>
<td>+21.4</td>
</tr>
<tr>
<td>5$^{th}$ - 6$^{th}$</td>
<td>0.0</td>
<td>+0.7</td>
<td>+6.4</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

We have analysed the electronic structure by plotting the DOS of both Zr$_{11}$Y$_{top}$O$_{24}$(111) and Zr$_{11}$Y$_{sub}$O$_{24}$(111) configurations in Figure 3-5 (a) and (b). The DOS demonstrates that independently of the Y position (either in the top or in the sub O-Zr-O trilayers) the composition of the $\alpha$ bands are similar to the pristine ZrO$_2$(111) surface. The bands just below the Fermi level correspond mainly to O$_u$ 2p orbitals. However, we note a $\beta$-state centred just over the Fermi level at 0.26 eV for Zr$_{11}$Y$_{top}$O$_{24}$(111) and 0.02 eV for Zr$_{11}$Y$_{sub}$O$_{24}$(111) (Figure 3-5 (c) and (d)). These $\beta$-states correspond to O$_u$ 2$p_y$ and O$_u$ 2$p_z$ orbitals at the surface for pristine ZrO$_2$(111) which appear just below the Fermi level (Figure 3-3 (a)). When the ZrO$_2$(111) surface is doped with Y, this dopant adopts an oxidation state maximum of +3 leading to a defective oxygen orbital rising above the Fermi level.
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Figure 3-5. (a) and (b) Density of states (DOS) of Zr$_{11}$Y$_{24}$O$_{24}$(111) and Zr$_{11}$Y$_{24}$O$_{24}$(111) configurations, respectively. (c) and (d) are the projected DOS of Zr$_{11}$Y$_{24}$O$_{24}$(111) and Zr$_{11}$Y$_{24}$O$_{24}$(111) respectively on O$_u$ atoms.

In Figure 3-6 (a) and (b) we show the charge density for the band energy of the unoccupied $\beta$-states, for the top and sub-layer doped systems, respectively. These charge density plots confirm graphically that the unoccupied $\beta$-states correspond mainly to O$_u$ 2$p_y$ and 2$p_z$ orbitals.
Figure 3-6. (a), (b) and (c) charge density plot of unoccupied β-states near the Fermi level of Zr$_{11}$Y$_{top}$O$_{24}$(111), Zr$_{11}$Y$_{sub}$O$_{24}$(111) and Zr$_{10}$Y$_{2}$O$_{24}$(111) respectively. Colour key: red, grey, and cyan spheres correspond to oxygen, Zr, and Y atoms, respectively.

3.3.2.2 Adsorption of Ni atom on Zr$_{11}$YO$_{24}$(111) surfaces

We have investigated twenty non-equivalent initial adsorption sites (Appendix-Figure 8-2, Table 8-2, Figure 8-3, and Table 8-3) for the deposition of a Ni atom on both Ni/Zr$_{11}$Y$_{top}$O$_{24}$(111) and Ni/Zr$_{11}$Y$_{sub}$O$_{24}$(111) surfaces (Figure 3-4 (c) and (d)). For each Y location (Ni/Zr$_{11}$Y$_{top}$O$_{24}$(111) and Ni/Zr$_{11}$Y$_{sub}$O$_{24}$(111)) the preferential adsorption site is over O$_d$', similar to the one found for the pristine ZrO$_2$(111) surface (Figure 3-4 (e) and (f)). However, when the zirconia surface is doped with Y, the O$_d$ linked to Y is not involved as the O$_d$' adsorption site. Indeed, for both configurations, Ni adsorbs on an O$_d$' site away from the Y atom.

The binding energy of Ni to Zr$_{11}$Y$_{sub}$O$_{24}$(111) (0.02 eV) is slightly lower than the binding energy found for Ni/Zr$_{11}$Y$_{top}$O$_{24}$(111) (0.05 eV) although the difference is negligible. Yet, Ni has more affinity for an Y-doped zirconia surface than for a pristine
surface by 2.4 eV, which is in good agreement with the charge analysis, where the charge of Ni on the YSZ surface is twice (0.6 e) that at the ZrO$_2$(111) surface, indicating more significant charge transfer.

The DOS of Ni/Zr$_{11}$Y$_{\text{sub}}$O$_{24}$(111) and Ni/Zr$_{11}$Y$_{\text{top}}$O$_{24}$(111) are presented in Figure 3-7 (a)-(b) and (c)-(d), respectively, which show that the DOS of the Ni/ZrO$_2$(111) interface is perturbed when the slab is doped with Y. Instead of five peaks with double electron occupation just below the Fermi level, as in Figure 3-3 (b), we note five $\alpha$-peaks and three $\beta$-peaks below the Fermi level and one $\beta$-peak above the Fermi level. The difference in the number of bands is related to different crystal field splitting of the Ni ad-atom owing to the presence of the Y-dopant.
Figure 3-7. (a) and (b) DOS of Ni/Zr$_{11}$Y$^{top}$O$_{24}$(111) and zoom peaks near the Fermi level, respectively. (c) and (d) DOS of Ni/Zr$_{11}$Y$^{sub}$O$_{24}$(111) and zoom peaks near the Fermi level, respectively.

The composition of the Ni/Zr$_{11}$Y$^{top}$O$_{24}$(111) α-peaks located just below the Fermi level. Figure 3-7 (b), shows an overlap of hybridized Ni s-d orbitals with surface atoms (O$_o$ and Zr near the ad-atom). Note also the negligible contribution of Y 4d to the α-peaks below the Fermi level, which is in good agreement with the observation made from Figure 3-4 (c): Ni prefers to interact with Zr rather than with Y. The presence of the β-peak over the Fermi level (composed mainly of Ni s-d and O$_o$ 2p orbitals) is due to the electron deficiency caused by the dopant Y, leading to partial unoccupied β-states (Figure 3-7 (b)). The Ni/Zr$_{11}$Y$^{sub}$O$_{24}$(111) DOS (Figure 3-7 (c)-
(d)) shows the same behaviour although the β-peak appears at higher energies, we suggest because of a stronger distortion of the crystal field on the O\textsubscript{u} atom.

Ni sits preferentially on an electron-deficient surface, obtained through doping with Y, but the most favourable site is away from the dopant. Moreover, charge analysis showed that the charge transfer between Ni and the surface is more important on the doped surface, in agreement with the electronic structure shown by the DOS, where d-states are isolated around the Fermi level.

### 3.3.2.3 Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{24} and VAC-Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{23} surfaces

We have also doped our ZrO\textsubscript{2}(111) slab with two Y atoms in order to obtain the optimized concentration of Y\textsubscript{2}O\textsubscript{3} in a ZrO\textsubscript{2} cermet of approximately 8%. As our surface formula is Zr\textsubscript{12}O\textsubscript{24}, substituting two Zr by two Y and removing one oxygen (VAC-Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{23}), leads to 9.1 % of the dopant, i.e. in the required range (8-10%) for the optimisation of the oxygen transport in the Ni/YSZ anode of the SOFC. Depending on the O chemical potential the SOFC anode (Ni/YSZ) can be enriched by oxygen thereby modifying the oxygen transport from the electrolyte (YSZ) to the anode and filling the oxygen vacancies (Shishkin & Ziegler 2008). We have therefore studied both Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{23} and Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{24}.

\[
(1-x)\text{ZrO}_2 + x\text{Y}_2\text{O}_3 \rightarrow \text{Zr}_{(1-x)}\text{Y}_2\text{O}_{(2+x)}
\]  

(3-2)

The VAC-Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{23}(111) slab (Figure 3-8 (a) and (b)) models the YSZ structures at low oxygen chemical potential, i.e. low oxygen pressure. The most stable configuration has the oxygen vacancy located at the next nearest neighbour (NNN)
site of the two Y atoms, in agreement with previous studies (Pietrucci et al. 2008; Xia et al. 2009). We have tabulated the relative energies for each configuration, (Appendix-Figure 8-1 and Table 8-1) and shown the most stable configuration in Figure 3-8 (a). In this configuration the Y were positioned in the top and the sub O-Zr-O trilayers, while the oxygen was removed from lower oxygen layer of the top O-Zr-O trilayer, to create the vacancy. This configuration is similar to one reported previously (Shishkin & Ziegler 2008; Chu et al. 2014; Chu et al. 2013).

We have also optimised the ZrO$_2$(111) surface doped with two Y atoms, without considering an oxygen vacancy, Zr$_{10}$Y$_2$O$_{24}$(111). We again substituted two Zr by Y in the same positions as found for the most stable configuration above, i.e. one belonging to the top O-Zr-O trilayer and the other one belonging to the sub trilayer (Figure 3-8 (c) and (d)). This slab thus models 9.1 % YSZ under high oxygen chemical potential i.e., oxidising conditions. During the SOFC operation, oxygen is transported through YSZ and this oxygen ion is assumed to occupy the oxygen vacancies (Shishkin & Ziegler 2008), hence our consideration of the Zr$_{10}$Y$_2$O$_{24}$(111) surface. As we perform our calculation using VASP, the charge is neutral. After geometric and electronic optimizations, we observe a charge rearrangement discussed in the next paragraph.
Figure 3-8. Side and top views of both YSZ(111) surfaces. (a) shows the side view of VAC-Zr\(_{10}\)Y\(_2\)O\(_{23}\)(111), (b) the top and the 38 non-equivalent initial adsorption sites for Ni atom. (c) shows the side view of Zr\(_{10}\)Y\(_2\)O\(_{23}\)(111), (d) the top and the 52 non-equivalent initial adsorption sites for Ni atom. (e) and (f) most stable adsorption site for Ni on VAC-Zr\(_{10}\)Y\(_2\)O\(_{23}\)(111) and Zr\(_{10}\)Y\(_2\)O\(_{23}\)(111), respectively. Colour key: red, grey, cyan and blue spheres correspond to oxygen, Zr, Y and Ni atoms, respectively. The oxygen vacancy is represented by an orange sphere.

Table 3-3 shows the distance evolution between the atomic layers when the ZrO\(_2\)(111) surface is doped with 2 Y atoms. The general trend observed is the increase of the inter-layer distances embedding the large volume of the Y atom.

Charge analysis did not show any substantial change after doping the ZrO\(_2\)(111) surface with two Y atoms. In the VAC-Zr\(_{10}\)Y\(_2\)O\(_{23}\)(111) system the only major change in terms of charges was observed for the oxygen near the vacancy which has a charge of -1.3 e while in the ZrO\(_2\)(111) it is charged at -1.2 e.

The DOS of Zr\(_{10}\)Y\(_2\)O\(_{24}\)(111) (Figure 3-9 (a)) shows one β-peak at the Fermi energy and another β-peak just above the Fermi level (0.37 eV). These peaks correspond
mainly to the β-unoccupied states of 2p\(_y\) and 2p\(_z\) orbitals of the oxygens surrounding the Y atoms (Figure 3-9 (b)). From the charge density plot of these band energies, Figure 3-6 (c), we suggested that the charges on the oxygens near the Y atoms are localised due to the electron deficiency. When one oxygen atom is removed (V\(_{\text{AC}}\)-Zr\(_{10}\)Y\(_2\)O\(_{23}\)(111) (Figure 3-8 (a) and (b)) there will be no electron deficiency (equation (3-2)) and the DOS therefore does not show the oxygen 2p unoccupied state (Figure 3-9 (c)).

Figure 3-9. (a) and (b) Density of states (DOS) and projected DOS of Zr\(_{10}\)Y\(_2\)O\(_{24}\)(111) configuration, respectively. (c) is the DOS of V\(_{\text{AC}}\)-Zr\(_{10}\)Y\(_2\)O\(_{23}\)(111).
3.3.2.4 Adsorption of Ni on YSZ

We compared the adsorption of Ni on both Ni/VAC-Zr$_{10}$Y$_2$O$_{23}$(111) (Figure 3-8 (e)) and Ni/Zr$_{10}$Y$_2$O$_{24}$(111) (Figure 3-8 (f)) surfaces. We investigated up to 52 nonequivalent initial Ni adsorption sites (Appendix-Figure 8-4 and Table 8-4) for the system under oxidising conditions and up to 38 configurations on VAC-Zr$_{10}$Y$_2$O$_{23}$(111) (Appendix-Figure 8-5 and Table 8-5).

On Ni/Zr$_{10}$Y$_2$O$_{24}$(111) (Figure 3-8 (f)), Ni prefers to adsorb away from the Y atoms and over an O$_{d}$' site, i.e., similar to the site found for Ni on the ZrO$_2$(111) surface doped with only one Y atom (Figure 3-4 (c) and (f)). The binding energy calculated for this adsorption is -1.65 eV which is stronger than the one found for the Ni/ZrO$_2$(111) (2.42 eV), Ni/Zr$_{11}$Y$_{top}$O$_{24}$(111) (0.05 eV) and Ni/Zr$_{11}$Y$_{sub}$O$_{24}$(111) (0.02 eV) configurations and energetically favourable. On the Ni/VAC-Zr$_{10}$Y$_2$O$_{23}$(111) surface, Ni adsorbs preferentially over the oxygen vacancy and away from the Y atoms (Figure 3-8 (e)). However, in previous investigations (Lustemberg et al. 2016), a discrepancy was found between the preferred adsorption of a metal ad-atom at the defect site on the oxide surface predicted by DFT and the actual result described by experiment. In their study, the authors (Lustemberg et al. 2016) deposited Au atoms on defective ceria (CeO$_{2-x}$) films and described the system using both STM and DFT. The STM results showed only a small number of Au atoms trapped in the oxygen vacancies, whereas the DFT calculations predicted a thermodynamically preferential adsorption at the defect site. Their STM results showed that at low temperature, i.e. 200 K, a negligible number of Au atoms sit on the oxygen vacancy. Even at 400 K, Au prefers to adsorb at the oxide step edge and away from the oxygen vacancy. The
reason behind this apparent discrepancy is the presence of diffusion barriers around the oxygen vacancy site that cannot be overcome by the ad-atom at moderate temperature. To confirm the importance of this kinetic effect, the authors used DFT calculations to evaluate the diabatic barrier heights (1.0 eV) and they showed that the diffusion of Au atoms towards the vacancy takes place only above 395 K. However, even at higher temperatures the diffusion of Au atoms could be blocked due to polaronic effects, as the adsorption of Au on an O vacancy requires a charge transfer.

Thus, our investigation could be complemented by similar STM experiments to evaluate if diffusion phenomena affect the preferential adsorption site for Ni on \( V\text{AC}-\text{Zr}_{10}\text{Y}_{2}\text{O}_{23}(111) \) which is the oxygen vacancy.

The binding energy of Ni on the \( V\text{AC}-\text{Zr}_{10}\text{Y}_{2}\text{O}_{23}(111) \) surface is weaker than in any other doped configurations, but slightly more favourable than on pristine \( \text{ZrO}_2(111) \).

Thus, at high concentrations of Y (9.1 %), Ni binds more strongly than at lower concentrations of dopant under oxidising conditions, i.e. when there is no oxygen vacancy, due to high electronic affinity of the system as shown by the DOS. This is consistent with the charge transfer from Ni to the surface when a Ni atom is adsorbed on the \( \text{Zr}_{10}\text{Y}_{2}\text{O}_{24}(111) \) surface (charge of Ni is 0.96 e). When the Ni is adsorbed on the \( V\text{AC}-\text{Zr}_{10}\text{Y}_{2}\text{O}_{23}(111) \) the charge found for Ni is 0.28 e, indicating that charge transfer is less significant when the surface contains oxygen vacancies.

These results would suggest that when the Ni/YSZ anode is enriched with oxygen (Shishkin & Ziegler 2008), corresponding to our \( \text{Ni/Zr}_{11}\text{Y}^{\text{top}}\text{O}_{24}(111) \), \( \text{Ni/Zr}_{11}\text{Y}^{\text{sub}}\text{O}_{24}(111) \) or \( \text{Ni/Zr}_{10}\text{Y}_{2}\text{O}_{24}(111) \) models, Ni metal particles would be more
stable at the surface than at the stoichiometric surfaces, e.g. Ni/VAC-Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{23}(111) or Ni/ZrO\textsubscript{2}(111).

**Figure 3-10.** (a) and (b) DOS of Ni/Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{24}(111) and detailed four peaks near the Fermi energy, respectively. (c) and (d) DOS of Ni/VAC-Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{23}(111) and detailed peaks near the Fermi energy, respectively.

**Figure 3-10** shows the density of states of Ni/Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{24}(111) and Ni/VAC-Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{23}(111). The oxidized surface (Ni/Zr\textsubscript{10}Y\textsubscript{2}O\textsubscript{24}(111)) shows an unoccupied \(\beta\)-state just above the Fermi level at 1.20 eV (**Figure 3-10 (a)**). This peak corresponds mainly to the unoccupied states of Ni 3d and O\textsubscript{u} 2p orbitals (**Figure 3-10 (b)**) which
is consistent with the charge transfer (Table 3-2). We also note the lack of Ni-s contribution to this band.

Under non-oxidising conditions YSZ (9.1 %) does not show any β-unoccupied band below the conduction band owing to the presence of an oxygen vacancy (Figure 3-10 (c)). The three α-peaks just below the Fermi energy of Ni/VAC-Zr_{10}Y_{2}O_{23}(111) (Figure 3-10 (d)) arise mainly from the Ni 3d, Ni 4s O_2p and Zr 4d orbitals, while the Y 4d orbital contributes weakly to these bands. It indicates a hybridization between Ni 3d and Ni 4s orbitals, which is not the case in the Ni/Zr_{10}Y_{2}O_{23}(111) configuration. The weak contribution of the Y 4d orbital to these peaks is consistent with the preferential adsorption of Ni away from the Y atom.

We have plotted in Figure 3-11 a positive and negative contour of the electron density difference as \( \Delta \rho = \rho_{\text{surface/Ni}} - (\rho_{\text{surface}} + \rho_{\text{Ni}}) \) for the five surfaces. It shows the electron density reallocation upon Ni deposition, which is in good agreement with the electronic analysis obtained from the DOS and the charges.
Chapter 3: Single Nickel adsorption on ZrO$_2$ and YSZ surfaces

3.4 Chapter conclusions

We have studied ZrO$_2$ with two Y dopant concentrations under both oxidizing and neutral conditions, and we have unravelled the electronic effects upon Ni deposition of 52 different initial adsorption sites on five surface configurations: ZrO$_2$(111), Zr$_{11}$Y$_{10}$O$_{24}$(111), Zr$_{11}$Y$_{10}$O$_{24}$(111), Zr$_{10}$Y$_2$O$_{24}$(111) and VAC-$Zr_{10}$Y$_2$O$_{23}$(111). We
have shown for each of the YSZ(111) surfaces, that doping with Y leads to an increase of the inter atomic layer distance because of the large ionic radius of Y comparing to Zr.

Ni adsorbs preferentially on a surface of high dopant concentration (9.1 %) under oxidising conditions because of the electronic affinity of the system. However, when YSZ (9.1 %) is under neutral conditions, the adsorption of Ni is still slightly more favourable than on the pristine ZrO$_2$(111).

From the electronic structure analysis (DOS, PDOS, charge and electron density difference) we conclude that the Ni atom always interacts with O$_u$, O$_d$ and Zr and adsorbs away from the Y when the surface is doped. When YSZ is stoichiometric, Ni adsorbs at the oxygen vacancy. Finally, charge transfer from Ni to the surface atoms takes place for all the systems considered.
Chapter 4

Ni sintering on ZrO$_2$ and YSZ surfaces

Abstract

The performance of supported metal catalysts, such as nickel nanoparticles decorating yttria stabilized, depends on the metal-support interface and their microstructure. The raising interest in a systematic study at the electronic structure level led us to describe, in this chapter, the interaction of Ni$_n$ clusters (n = 1-10) supported on c-ZrO$_2$(111) and YSZ(111), using spin polarized density functional theory (DFT) including long-range dispersion forces. We have evaluated different cluster geometries and determined the electronic structure of the most stable configurations. Our results show that the clusters prefer to adopt a three dimensional structure on both surfaces. The interfacial interaction is characterized by a charge transfer from the cluster to the surface. We have also shown how yttrium, present in YSZ, affects the Ni-Ni interaction. By analysing the difference between the cohesive energy and the clustering energy, we show the preference of Ni-Ni bond formation over Ni-surface interaction; this energy difference decreases with the increase of the Ni$_n$ cluster size. From the evaluation of the Ni atomic hopping rates, we have demonstrated that Ni atom aggregates to other atoms or bigger clusters, under different temperature conditions, on both ZrO$_2$(111) and YSZ(111) surfaces, affecting the cluster size stability.
Chapter 4: Ni sintering on ZrO$_2$ and YSZ surfaces

4.1 Introduction

In the previous chapter we have described the adsorption of one single Ni atom on top of ZrO$_2$(111) and YSZ(111) surfaces which enlightened us about the preference adsorption site of metal atom on those oxide surfaces. The geometry described in chapter 3 will be therefore the starting point of the construction of Ni cluster on top of ZrO$_2$(111) and YSZ(111) surfaces. Considering several Ni atoms rather than a single one allow us to better describe the metal-oxide interface and model certain phenomena observed experimentally such as the aggregation of Ni atoms on top of the surface which affects the performance of the solid oxide fuel cell (SOFC). Indeed, the catalytic activity of the surface is directly linked to the nature of the metal-support interaction (Catlow et al. 2003) and hence our interest in Ni/ZrO$_2$ and Ni/YSZ interfaces.

While experimentation information of the metal-oxide interface is difficult to obtain at the atomic level, computational tools provide crucial insights (J. Li et al. 2013; Ogura, T., Nakao, K., Ishimoto, T., and Koyama 2011). Methods based on the density functional theory (DFT) are suitable for the description of metal-oxide interfaces (Teng et al. 2012), but it is a time-consuming method and in this work we have therefore focused on the study of the adsorption of small clusters (Ni$_{1-5}$) on the ZrO$_2$(111) surface to provide fundamental insight into the Ni/ZrO$_2$(111) interaction. Other authors have used DFT to study related metal-oxide interfaces. For instance, Catlow et al. (Catlow et al. 2003) have investigated the deposition of palladium and platinum layers on zirconia and ceria surfaces and found that the electronic configuration of the noble metal is determined by the metal support interaction. Li et
al. (Li et al. 2011) studied the deposition of an Au\textsubscript{10} cluster on the MgO (111) surface and demonstrated charge transfer from the cluster to the surface. Molina et. al. (Molina & Hammer 2005) have shown that Au\textsubscript{20} cluster keeps tetrahedral geometry upon adsorption on the MgO(100) surface. Di Valentin et al. investigated the stability and growth of Ni cluster on the MgO surface (Di Valentin et al. 2003) where small Ni\textsubscript{n} (n ≤9) clusters adsorb weakly on the surface and their diffusion can be stopped by surface defect such as oxygen vacancies. Teng et al. (Teng et al. 2012) deposited Au\textsubscript{x} (x=1-10) on the stoichiometric and partially reduced CeO\textsubscript{2} (111) surfaces and showed that the stability of Au\textsubscript{x} clusters depends on the surface structure and the Au-Au bond strength and arrangement. Jiang et al. (Jiang et al. 2012) used DFT to investigate the geometric structure of Pt\textsubscript{n}(n = 4-8) clusters on the TiO\textsubscript{2}(110) surface. They found that Pt\textsubscript{4} adopts a flat geometry upon adsorption, while Pt\textsubscript{n}(n = 5-8) adopts a two-layer structure where only the bottom layer interacts with the support. Luches et al. (Luches et al. 2012) characterized by STM and X-ray photoelectron spectroscopy (XPS) measurements the nucleation and growth of Ag nanoparticles on CeO\textsubscript{2}(111). They have also complemented their experimental results with DFT calculations, where they showed charge transfer from the Ag clusters to the ceria surface. Hahn et al. (Hahn et al. 2015) used DFT to study the adsorption of Ni clusters on top of CeO\textsubscript{2}(111) and showed that the metal cluster is stabilized as the cluster size increases (up to ten atoms). Ma et al. (Ma et al. 2013) in their investigation of the nucleation and aggregation processes of Ag atoms on the AgCl (100) surface demonstrated that the clusters are thermodynamically more stable than layered structures with the stability increasing with the cluster size. Jung et al. (Jung et al. 2006) described the interaction...
of CO with M (M=Pd and Pt) supported on c-ZrO$_2$(111), although these authors were more focused on the effect of M/ZrO$_2$(111) on CO adsorption rather than on the M-ZrO$_2$ interaction itself.

Finally, other density functional theory (DFT) investigations studied the interaction of certain metals on γ-Al$_2$O$_3$ (Cao et al. 2011; Briquet et al. 2009; Mei et al. 2010; Liu et al. 2010). Rajesh et al. (Rajesh et al. 2014) studied the adsorption of Au$_n$ (n = 2-10) on α-Al$_2$O$_3$ (0001) showing a favourable metal clustering instead of spreading across the surface, i.e. wetting.

A systematic study of the influence of Ni cluster size and configuration on the Ni/ZrO$_2$ and Ni/YSZ interface is still lacking and in this work we have therefore analysed the interaction of Ni$_n$ (n=1-10) clusters with the c-ZrO$_2$ (111) and YSZ(111) surfaces, showing the effect of the cluster configuration on the binding process. We have also analysed the electronic structure of the Ni$_n$/ZrO$_2$(111) and Ni/YSZ(111) interfaces to describe the electronic rearrangement of the surface atoms caused by the metal cluster. Finally, we have calculated the hopping rate to gain insight into the diffusion of Ni atoms on the c-ZrO$_2$(111) and YSZ(111) surfaces.

### 4.2 Models and computational methods

We have performed the DFT (Hohenberg & Kohn 1964) calculations using the Vienna Ab-initio Simulation Package (VASP) (Kresse & Furthmüller 1996b; Kresse & Furthmüller 1996a; Kresse & Hafner 1993; Kresse & Hafner 1994) which solves the Kohn-Sham equations in a periodic approximation. The exchange-correlation
functional was approximated using the generalized gradient approximation (GGA) (Perdew et al. 1996) with the Perdew-Burke-Ernzerhof (PBE) density functional. The long-range dispersion interactions were described by the semi-empirical method of Grimme (Grimme 2006). The O (2 s, 2 p), Ni (3 d, 4 s), Zr (4 d, 5 s) and Y (4 s 4p 4 d 5 s) atomic orbitals have been treated as valence electrons and their interaction with the remaining frozen core electrons was described by the projected augmented wave method (PAW) (P E Blöchl 1994). For the ZrO$_2$ bulk calculations the reciprocal space was described by Monkhorst-Pack grids with 9x9x9 mesh of k-points. For the 1x1 slab calculations a 7x7x1 mesh of k-points was used, while for the 2x2 slab calculations a 3x3x1 mesh of k-points was adopted.

The METADISE code (Watson et al. 1996) was used to generate the ZrO$_2$(111) surface, where the atomic charges and the periodicity in the plane direction are taken into account. This code allowed us to obtain a stacking of the atomic layers resulting in a zero dipole moment perpendicular to the surface plane, although this particular surface we could also have obtained by using the electron counting method (Santos-Carballal et al. 2014). Different surface terminations have been investigated and the most stable determined here was the O-terminated ZrO$_2$ (111), in agreement with previous studies (Grau-crespo et al. 2007; Cadi-Essadek et al. 2015).

As in chapter 3, a slab model was considered to define the surfaces and the vacuum size was set to 15 Å in order to avoid perpendicular interactions. Nine atomic layers (three O-Zr-O trilayers) in the z-direction were adopted for the slab thickness. The top five atomic layers were allowed to relax during geometry optimization, while the
bottom four layers were kept fixed at their bulk equilibrium position to represent the rest of the crystal. We adopted the same YSZ model as in the previous chapter, i.e. we substituted 2 Zr by 2 Y atoms and removed one oxygen in order to obtain the yttria stabilized zirconia (YSZ) surface with a dopant concentration of 9.09%, which is in the range of an optimized oxygen transport YSZ electrode (8-10 %). Both ZrO$_2$(111) and YSZ(111) surfaces are presented in Figure 4-1.

Figure 4-1. (a) and (b) represent the side and the top view, respectively, of the oxygen terminated ZrO$_2$(111) surface. (c) and (d) correspond to the side and top view, respectively, of the YSZ(111) surface. Colour key: O, Zr, and Y are respectively represented by a red, grey, and cyan sphere. The yellow sphere corresponds to the oxygen vacancy.
For the adsorption of one Ni atom on the surface, a 1x1 slab was considered, which contains 36 atoms (four atoms per atomic layer) and has a surface area of 44.96 Å². When we adsorbed more than one Ni on the surface, a 2x2 slab was considered to avoid lateral interactions between Ni clusters. Thus, the 2x2 slab contains 144 atoms (sixteen atoms per atomic layer) and has a surface area of 179.84 Å².

There are many possible shapes and adsorption sites for Ni_n clusters. We have chosen the Ni_n geometries based on the stability of fcc Ni surfaces (Liu et al. 2011; Jung et al. 2006; Li et al. 2011; Ma et al. 2013) and small particles (Roldan et al. 2009) in agreement with previous studies. We have therefore grown Ni(111)-facet (Li et al. 2014; Hong et al. 2002) exposing clusters on ZrO_2(111) and YSZ(111) surfaces where the initial atomic spacing between the Ni atoms is 2.2 Å, similar to the interatomic distance in the Ni(111) surface. Concerning the adsorption sites, we have based the initial positions of our clusters on our previous findings described in (Cadi-Essadek et al. 2015). On the ZrO_2(111) surface, Ni adsorbs on O_d’ (slightly off from the perpendicular) (Figure 4-1 (a) and (b)) and interacts with the oxygen surface atoms. On the YSZ(111) surface, Ni atom adsorbs preferentially on top of the oxygen vacancy, away from the Y atoms (Cadi-Essadek et al. 2015). Thus, we have grown the Ni_n(n=2-10) clusters away from the Y atoms.

To describe the interaction of the Ni clusters with the surface we have calculated the clustering energy per Ni atom as follow (equation (3-1)):
Chapter 4: Ni sintering on ZrO$_2$ and YSZ surfaces

\[ E_{\text{clus}} = \frac{E_{\text{Ni}_n/\text{surf}} - (E_{\text{surf}} + nE_{\text{Ni}})}{n} \quad (4-1) \]

where \( E_{\text{Ni}_n/\text{surf}} \), \( E_{\text{surf}} \) and \( E_{\text{Ni}} \) are the energies of the slab with the \( n \) Ni atoms adsorbed on the surface, the clean oxide surface and the Ni metal atom, respectively, and \( n \) is the number of adsorbed Ni atoms. A positive clustering energy means that Ni atoms prefer to aggregate rather than wet the surface, whereas a negative clustering energy indicates that the Ni atoms prefer to spread over the surface.

We have also calculated the cohesive energy of the metal cluster configurations (equation \( 3-1 \)):

\[ E_{\text{coh}} = \frac{E_{\text{Ni}_n} - nE_{\text{Ni}}}{n} \quad (4-2) \]

where \( E_{\text{Ni}_n} \) is the energy of the Ni$_n$ cluster. To calculate \( E_{\text{Ni}_n} \) we first optimized Ni$_n$/surf, then removed the surface and performed a single point calculation of the Ni$_n$ geometry as in the optimized Ni$_n$/surf system. Finally, we have described the perpendicular interactions between the surface and the Ni clusters from the interaction energy (equation \( 4-3 \)):

\[ E_{\text{int}} = \frac{E_{\text{Ni}_n/\text{surf}} - (E_{\text{surf}} + E_{\text{Ni}_n})}{n_{\text{c}}} \quad (4-3) \]

where \( E_{\text{surf}} \) is the energy of the geometry of the clean oxide surface taken from the optimized Ni$_n$/surf structure and \( n_{\text{c}} \) is the number of Ni atoms in contact with the surface. To calculate \( E_{\text{surf}} \), we first optimized Ni$_n$/surf, then removed the Ni$_n$ cluster and performed a single point calculation of the surface geometry as it is in the optimized Ni$_n$/surf system.
4.3 Ni\textsubscript{n}/ZrO\textsubscript{2}(111) (n=1-5): structural analysis

4.3.1 Ni\textsubscript{1}/ZrO\textsubscript{2}(111)

Before describing the interaction of Ni\textsubscript{n} (n=1-10) clusters with the zirconia surface, we need to remind how a single Ni atom affects the geometric and electronic structures of the oxide surface as the adsorption of one Ni is the starting point of the construction of the clusters.

In chapter 3, we studied the adsorption of one Ni atom on the ZrO\textsubscript{2}(111) surface. We considered seven different initial adsorption sites for the Ni atom on the O-terminated ZrO\textsubscript{2}(111). We also stated in chapter 3 that Ni adsorbs preferentially on top of O\textsubscript{d}' (slightly off from the perpendicular) (Figure 4-1) with a clustering energy of 2.42 eV. From Figure 4-2 we note that Ni interacts with the two nearest O\textsubscript{u} atoms causing a movement of those two surface atoms away from their initial positions. Indeed, the O\textsubscript{u}-O\textsubscript{u} distance is 3.603 Å for the clean surface, which becomes 3.708 Å upon Ni adsorption due to the interaction between Ni and the oxygen surface. This interaction between a Ni atom and the oxygen in the zirconia surface has also been shown by Choi et al. (Choi et al. 2016) who have employed DFT calculations to study the adsorption of a Ni atom on top of both m-ZrO\textsubscript{2}(\overline{1}11) and an ultrathin zirconia surface (ZrO\textsubscript{2} trilayer on Pt(111)). On m-ZrO\textsubscript{2}(\overline{1}11), the Ni atom is adsorbed on top of an O-O bridge position with a binding energy of 2.71 eV. The geometry of Ni/m-ZrO\textsubscript{2}(\overline{1}11) is similar to the one described in Figure 4-2 a), where the ad-atom interacts with both O\textsubscript{u} surface atoms. Furthermore, Choi et al. (Choi et al. 2016) found that the Ni is 1.82 and 1.88 Å away from the nearest oxygen surface atoms and 2.34 Å from the nearest Zr atom. Those interatomic distances are similar to the ones found in our investigation, i.e. an
average of 1.957 Å for the Ni-Oₐ distances and 2.355 Å for the Ni-Zr distance. On the ultrathin film the Ni adsorption was stronger and the Ni atom transferred more charge to the surface.

![Figure 4-2](image.png)

**Figure 4-2.** (a), (b), (c), (d), (e) and (f) side view of Ni₁/ZrO₂(111), Ni₂/ZrO₂(111), Ni₃/ZrO₂(111), flat- Ni₄/ZrO₂(111), pyr- Ni₅/ZrO₂(111) and Ni₆/ZrO₂(111) systems, respectively. Colour key: red, grey, and blue spheres correspond to oxygen, Zr and Ni atoms, respectively.

The analysis of the Bader charges (**Table 4-1**) shows the effect of Ni on the electronic structure of the surface atoms. Upon adsorption, the charge of the Oₐ and Zr atoms nearest the Ni is modified, from -1.2 to -1.1 e and from 2.3 e to 2.1 e for Oₐ and Zr, respectively. Ni has obtained a charge of +0.3 e, showing a slight oxidation of metallic Ni due to the charge transfer to the surface which causes the electronic rearrangement of the Oₐ and Zr atoms.
Table 4-1. Calculated energies, charges and d-band center position for the most stable configuration of the 5 systems.

<table>
<thead>
<tr>
<th></th>
<th>Ni$_1$/ZrO$_2$(111)</th>
<th>Ni$_2$/ZrO$_2$(111)</th>
<th>Ni$_3$/ZrO$_2$(111)</th>
<th>flat-Ni$_4$/ZrO$_2$(111)</th>
<th>Ni$_5$/ZrO$_2$(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{	ext{clus}}$</td>
<td>2.42</td>
<td>2.16</td>
<td>1.77</td>
<td>1.57</td>
<td>1.53</td>
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<td>$E_{	ext{coh}}$</td>
<td>--</td>
<td>3.83</td>
<td>3.38</td>
<td>3.11</td>
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<td>-2.05</td>
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<th>Ni$_3$/ZrO$_2$(111)</th>
<th>flat-Ni$_4$/ZrO$_2$(111)</th>
<th>Ni$_5$/ZrO$_2$(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
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<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Ni$_1$/ZrO$_2$(111)</th>
<th>Ni$_2$/ZrO$_2$(111)</th>
<th>Ni$_3$/ZrO$_2$(111)</th>
<th>flat-Ni$_4$/ZrO$_2$(111)</th>
<th>Ni$_5$/ZrO$_2$(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
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<td>-1.18</td>
<td>-1.18</td>
<td>-1.29</td>
<td>-1.73</td>
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</table>

We have plotted the electron density difference as $\Delta \rho = \rho_{\text{Ni/surface}} - (\rho_{\text{surface}} + \rho_{\text{Ni}})$ in Figure 4-3, showing the orientation of the atomic orbitals, from which a gain of electron density between Ni and the surface atoms is clearly seen. For instance, a charge accumulation is observed between the Ni and Zr atoms, confirming the electronic rearrangement described by the Bader analysis, with the atomic orbitals of O$_u$ atoms pointing towards the Ni adatom. In addition, Figure 4-3 displays charge depletion around the Ni atom.

After this reminder on the electronic and geometric structures of Ni$_1$/ZrO$_2$(111) we can expose the results describing the Ni$_n$/ZrO$_2$(111) (n=1-10) interaction.
4.3.2 Ni$_n$/ZrO$_2$(111) n=(2-5)

As it is difficult to consider all possible configurations of the Ni$_n$ clusters, we will build the clusters incrementally with the shape and the initial adsorption sites based on our Ni$_1$/ZrO$_2$(111) findings above and previous investigations in the literature of similar systems, i.e. metal clusters supported on oxide materials (Liu et al. 2011; Jung et al. 2006; Li et al. 2011; Ma et al. 2013).

We identified in the previous section that Ni is preferentially positioned on top of the O$_d$’ site, where it interacts mainly with its nearest O$_u$ and Zr neighbours. Therefore, the atoms of the cluster facing the surface are initially positioned near the O$_u$ atoms and on top of the O$_d$’ site. The other consideration taken into account in the Ni$_n$/ZrO$_2$(111) interfaces is the cluster shape. Since in the metal, the Ni(111) is the most stable surface (Li et al. 2014; Hong et al. 2002), Ni(111)-facetted clusters have
been adsorbed on the metal oxide surface. Thus, the initial atomic spacing in the Ni\textsubscript{n} clusters corresponds to the one in the Ni(111) metal surface, i.e. 2.2 Å, although all atoms in the Ni clusters as well as the surface zirconia layers are allowed to move and relax freely during the geometry optimization.

The first cluster studied here is Ni\textsubscript{2} which adsorbs on the ZrO\textsubscript{2}(111) surface with a clustering energy of 2.16 eV. Ni\textsubscript{a} and Ni\textsubscript{b} (Figure 4-2 (b)) were initially positioned at 2.650 Å and 2.466 Å, respectively, from their nearest O\textsubscript{u} neighbor. After geometry optimization, we note a decrease of the Ni-O\textsubscript{u} distance: Ni\textsubscript{a}-O\textsubscript{u} = 1.753 Å and Ni\textsubscript{b}-O\textsubscript{u} = 1.813 Å. Additionally, each O\textsubscript{u} has moved away from its initial position, similar to the observation made for Ni\textsubscript{1}/ZrO\textsubscript{2}(111): the final O\textsubscript{u}-O\textsubscript{u} distance observed for Ni\textsubscript{2}/ZrO\textsubscript{2}(111) is 4.621 Å whereas it is 3.603 Å for the clean surface. This effect of the interaction of Ni\textsubscript{2} with surface atoms can be confirmed further by evaluating the charge of the cluster and the relevant surface atoms.

The analysis of the Bader charges shows a decrease of 0.1 e in the negative charge of both O\textsubscript{u} atoms interacting with Ni\textsubscript{2}. The positive charge of the Zr atom is decreased by 0.2 e and the sum of the cluster charge is +0.2 e. This electronic rearrangement is visualized in the electron density difference plot (Figure 4-3) where we have an obvious charge accumulation between Ni\textsubscript{2} and the surface. In addition, the orbitals of the two O\textsubscript{u} interacting with the adatoms are well localized and pointing towards Ni.

The second cluster considered here is Ni\textsubscript{3}/ZrO\textsubscript{2}(111) where the cluster adsorbs on the surface with a clustering energy of 1.77 eV. After geometry optimization, the final shape of the Ni\textsubscript{3} cluster is a triangle where each Ni interacts with its nearest O\textsubscript{u}
neighbours, similarly to the metal-surface interactions of the Ni$_1$ and Ni$_2$ clusters. Each Ni atom is positioned at 1.8 Å from its nearest O$_u$ neighbour, whereas before geometry optimization the average Ni-O$_u$ distances was 2.3 Å. We also observe in the Ni$_3$/ZrO$_2$(111) system a shift of the O$_u$ atom positions, in the surface plane, as was found for Ni$_1$/ZrO$_2$(111) and Ni$_2$/ZrO$_2$(111). Moreover, the centre of the Ni$_3$ triangle is positioned over the Zr surface atom to optimize the interaction with it. This interaction is confirmed by the Bader charge analysis, since the charge on this Zr atom is +2.0 e while it is +2.3 e for the clean surface. We also note an average decrease of 0.1 e in the negative charge of the O$_u$ atoms (nearest neighbors of Ni) upon Ni$_3$ adsorption: -1.1 e for Ni$_3$/ZrO$_2$(111) while it is -1.2 e for the clean ZrO$_2$(111) surface. Finally, the total charge of the Ni$_3$ cluster is +0.3 e, indicating that charge transfer to the surface takes place, which explains the electronic rearrangement observed for O$_u$ and Zr.

The analysis of the electron density difference plot (Figure 4-3) shows this modest charge transfer from Ni$_3$ cluster to the surface, since we observe an accumulation of charge between the cluster and the Zr atom located under the cluster. Another accumulation of charge is observed between each Ni atom and its nearest O$_u$ neighbour, whereas in the meantime a depletion of charge is observed around each Ni atom.

The third cluster considered in this investigation is Ni$_4$/ZrO$_2$(111) where the clustering energy of the most stable configuration (Figure 4-2 (d)) is 1.57 eV. This flat configuration is slightly more favourable than the pyramid one (Figure 4-2 (e), 1.62 eV), since in flat-Ni$_4$/ZrO$_2$(111) the Ni-O$_u$ interactions are maximized which stabilizes
the Ni$_4$ cluster. In terms of the total energy, the flat configuration is 0.23 eV more stable than the three dimensional cluster. Indeed, in the flat configuration we have 4 Ni interacting with 4 O$_u$ while in the pyramid shape only 3 O$_u$ are involved in the interaction with the Ni$_4$ cluster. Thus, we focus here only on the flat shape and it can be seen from Figure 4-2 (d) that upon adsorption the nearest O$_u$ atoms to the cluster are pushed away from their initial positions, where the average distance between each Ni and its neighbouring O$_u$ is 1.8 Å as it was in Ni$_2$/ZrO$_2$(111) and Ni$_3$/ZrO$_2$(111).

Bader charge analysis shows that flat-Ni$_4$/ZrO$_2$(111) behaves similarly to Ni$_2$/ZrO$_2$(111) and Ni$_3$/ZrO$_2$(111): upon Ni$_4$ adsorption, the Ni$_4$ cluster becomes positively charged (+0.4 e), the negative charge of O$_u$ (nearest neighbors of Ni) decreases by 0.1 e and the positive charge of Zr (nearest neighbor of Ni) decreases by +0.3 e. Thus, a charge transfer from the cluster to the surface is responsible for the electronic rearrangement of the surface atoms.

The electron density difference plot of Ni$_4$/ZrO$_2$(111) (Figure 4-3) shows an important accumulation of charge between the cluster and the nearest Zr belonging to the surface. We also note that the O$_u$ atomic orbitals are well localized and pointing towards their respective Ni neighbor. Finally, a depletion of charge surrounding each Ni atom is observed.

The last cluster we have considered is Ni$_5$/ZrO$_2$(111). Again, we have considered two initial shapes for Ni$_5$/ZrO$_2$(111): flat and pyramidal. However, after geometry optimization, the flat Ni$_5$ configuration converged to a shape similar to the pyramid configuration (shown in Figure 4-2 (f)) with a clustering energy of 1.88 eV. Therefore, whatever the initial shape of the Ni$_5$ cluster, the 5 Ni adatoms tend to adopt a pyramid
shape on top of the zirconia surface. The most stable pyramid shape found is shown in Figure 4-2 (f) and the clustering energy calculated for this configuration is 1.53 eV. Therefore, in the optimized structure of Ni₅, we have 4 Ni atoms exposing a (111) face to the zirconia surface and interacting with the Oᵤ atoms. One Ni atom is positioned on top of the 4 Ni to form the pyramid. Oᵤ atoms act like a trap for the cluster since in Ni₅/ZrO₂(111) the Ni interacting with Oᵤ atoms are oriented toward them with an average distance of 1.8 Å and Oᵤ are pushed away from their initial position, similarly to the previous configurations (Ni₄/ZrO₂(111), Ni₃/ZrO₂(111), Ni₂/ZrO₂(111) and Ni₁/ZrO₂(111)).

Bader charge analysis shows the same behaviour as in the adsorption of the smaller clusters: the negative charge of Oᵤ interacting with Ni decreases from -1.2 e to -1.1 e upon cluster adsorption; the positive charge of the Zr atom near the cluster decreases from 2.3 e to 2.0 e. Finally, the Ni₅ adsorbed cluster has a charge of +0.4 e explaining the electronic rearrangement observed in the zirconia atoms. The charge lost by the cluster is partially accumulated between the cluster and the surface and affects the electron localization of the surface atoms. The electron density difference plot of Ni₅/ZrO₂(111) (Figure 4-3) shows this charge accumulation between the cluster and the nearest Zr. It also shows the orientation of the Oᵤ atomic orbitals, which are again localized and pointing towards Ni atoms.

4.4 Ni diffusion on ZrO₂(111)

The general trend of the interaction of the five clusters (Ni₁₋₅) with the surface shows that the Ni atoms interact mainly with Oᵤ and Zr. When the number of Ni in the cluster
is > 2, the Ni cluster shape is a (111)-facet and the cluster is positioned in a way to maximize its interaction with O_u and Zr atoms. Figure 4-4 shows that the clustering energy is proportional to the size of the adsorbed Ni cluster: the larger the cluster, the lower $E_{\text{clus}}$, i.e. the trend of Ni clusters on ZrO$_2$(111) indicates that aggregation of the Ni atoms is preferred over dispersion of individual atoms across the surface.

![Figure 4-4](image)

**Figure 4-4.** Calculated clustering energy ($E_{\text{clus}}$ / eV) for different Ni$_n$ clusters adsorbed on ZrO$_2$ (111). We show here the most stable configurations.

Furthermore, we note from Table 4-1 that the difference between $E_{\text{clus}}$ and $E_{\text{coh}}$ decreases with the increase of the cluster size, due to the decrease of the ratio of interaction between metal atoms and the surface for larger clusters. Therefore, the cluster-surface interaction contributes weakly to the clustering energy. A similar result
was found by Ma et al. (Ma et al. 2013) in their investigation of the adsorption of Ag clusters on the AgCl (100) surface.

$E_{\text{int}}$ decreases with cluster size (Table 4-1) which is predictable since for larger clusters there are more atoms in contact with the surface, leading to an augmentation of perpendicular Ni-surface interactions. We also note from Table 4-1 that the d-band centre decreases with the increase of the cluster size.

We have next evaluated the activation energy of diffusion of one Ni towards the Ni$_4$ cluster on top of ZrO$_2$(111) surface (Figure 4-5), by identifying the transition state along the diffusion pathway using the dimer method (Heyden et al. 2005).

![Figure 4-5](image)

**Figure 4-5.** Energy profile showing (Ni+Ni$_4$)/ZrO$_2$(111) and Ni$_5$/ZrO$_2$(111) states separated by a transition state. Colour key: red, grey, and blue spheres correspond to oxygen, Zr and Ni atoms, respectively.

**Figure 4-5** shows that the configuration Ni$_5$/ZrO$_2$(111) is more stable than (Ni+Ni$_4$)/ZrO$_2$(111), which indicates that the Ni atoms prefer to aggregate rather than
be dispersed on the surface, which is in good agreement with the clustering energies calculated in the previous section. The energy difference between the transition state and (Ni+Ni$_4$)/ZrO$_2$(111) structures, i.e. the activation energy, is equal to 0.72 eV. Thus, using this activation energy ($\Delta E = 0.72$ eV), we can calculate the hopping rate from state (Ni+Ni$_4$)/ZrO$_2$(111) to state Ni$_5$/ZrO$_2$(111) of the Ni atom:

\[ k_{A \rightarrow B} = \nu \exp \left( -\frac{\Delta E}{k_B T} \right) \]

where A is state (Ni+Ni$_4$)/ZrO$_2$(111) and B is state Ni$_5$/ZrO$_2$(111). The Boltzmann constant $k_B = 1.37789 \times 10^{-5}$ eV K$^{-1}$ and the vibrational frequency $\nu$ is approximately equal to $10^{12}$ s$^{-1}$. $k_{A \rightarrow B}$ is then calculated for a range of temperatures, corresponding to the working temperature of the SOFC ($T = 500^\circ$C-900$^\circ$C).

*Figure 4-6* shows that this $k_{A \rightarrow B}$ varies from $1.87 \times 10^7$ to $7.66 \times 10^8$ s$^{-1}$, indicating that Ni diffusion on the ZrO$_2$ (111) surface occurs under the experimental conditions.
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4.5 Conclusions on Ni$_n$/ZrO$_2$(111) (n=1-5) interaction

We have studied the interaction of five Ni$_n$ (n=1-5) clusters with the ZrO$_2$(111) surface, where we have shown that the clustering energy decreases with increasing Ni cluster size. The clustering energy was positive for all clusters, indicating that Ni atoms prefer to aggregate rather than wet the surface. When the number of Ni in the cluster is > 2, the Ni cluster shape is a (111)-facet and the cluster is positioned in such a way to maximize its interaction with O$_u$ and Zr atoms. From the electronic structure analysis (charges and electron density differences) we have demonstrated that Ni clusters transfer charge to the surface, which affects the electronic structure of O$_u$ and Zr atoms: there is an accumulation of charge between Ni and the surface atoms and the atomic orbitals of O$_u$ are well localized and point towards Ni. Finally, from clustering and cohesive energy calculations, diffusion barrier and hopping rates it can be concluded that nucleation of clusters of Ni atoms can take place on the ZrO$_2$(111) surfaces under the experimental conditions specific to the applications of SOFC.

The aim of the next section is to consider larger Ni$_n$ (n=6-10) clusters adsorption on ZrO$_2$(111) in order to validate our findings considering small Ni$_n$ cluster sizes (n=1-5). We will also compare the Ni$_n$/ZrO$_2$(111) (n=1-10) interaction with the Ni$_n$/YSZ(111) (n=1-10) in order to understand the influence of the Y dopant on the Ni$_n$ adsorption.
4.6 Ni\textsubscript{n}/ZrO\textsubscript{2}(111) (n = 6-10) and Ni\textsubscript{n}/YSZ(111) (n=1-10): structural analysis

4.6.1 Ni\textsubscript{n}/ZrO\textsubscript{2}(111) (n=6-10)

Based on the findings above, we have positioned up to Ni\textsubscript{10} by maximizing the interactions with O\textsubscript{u} surface atoms and considered flat and pyramidal morphologies. For example, we have tried four initial configurations for the Ni\textsubscript{6} cluster on ZrO\textsubscript{2}(111) (Appendix-Figure 8-6): one flat and two in three dimensional shape. The most stable shape has five Ni atoms at the basis of a pyramid, see Figure 4-7, maximising their interaction with the O\textsubscript{u} atoms and having an $E_{\text{clus}}$ of 1.51 eV. The average Ni-Ni distance in this cluster is 2.4 Å, which is 0.2 Å shorter than those in the Ni(111) surface. The optimized structure is different from the initial guess, where before relaxation the Ni atoms were positioned in a flat distribution in contact with the surface. After relaxation, the atoms adopted a Ni(111)-facetted tetrahedron shape on the zirconia surface. Similar studies (Rajesh et al. 2014; Zhang et al. 2014) on metal-support interactions have also shown that metal clusters prefer to adopt a 3D configuration on oxide surfaces beyond a critical number of atoms.
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Table 4-2. Calculated clustering ($E_{\text{clus}}$), cohesive ($E_{\text{coh}}$) and perpendicular interaction ($E_{\text{int}}$) energies (in eV), and Ni$_a$ charges (e) of the most stable configuration of both Ni$_a$/ZrO$_2$(111) and Ni$_a$/YSZ(111) systems. Ni$_a$/ZrO$_2$(111) (n=2-5) values are taken from the previous section for comparison.

#### ZrO$_2$(111)

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<tr>
<th>Configuration</th>
<th>$E_{\text{clus}}$</th>
<th>$E_{\text{coh}}$</th>
<th>$E_{\text{int}}$</th>
<th>Total Ni$_a$ charge</th>
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<td>Ni$_5$/ZrO$_2$(111)</td>
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#### YSZ(111)

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The analysis of the interface distances in the Ni₆/ZrO₂(111) system shows that each Ni is at ~1.9 Å from its nearest Oₜ neighbour. In addition, we note that these Oₜ atoms are shifted from their initial position: the Oₜ-Oₜ distance is 3.6 Å in the clean ZrO₂(111) surface whereas it is approximately 4.1 Å upon Ni₆ adsorption. The Oₜ atoms are pushed apart in order to accommodate the cluster and minimise the forces on it. The adsorption of this cluster also affects the electronic structure of ZrO₂. We have evaluated the atomic charges (Table 4-2) and observed a total charge transfer of 0.5 e from the metal cluster to the surface. The charge transfer is slightly higher for the Ni₉ and Ni₁₀ clusters: +0.6 and +0.7 e, respectively.
This charge transfer causes an electronic rearrangement of the surface atoms interacting with the cluster: the negative charge of the O atoms decreases from -1.2 to -1.1 e, while the charge of the Zr atoms (near the cluster) decreases from 2.3 to 2.1 e. We have also noted that only the five Ni atoms directly bonded to the surface transfer charge to ZrO$_2$(111), since each of those Ni atoms are +0.1 e while the Ni atom at the top of the cluster remains uncharged. Generally, Ni atoms at the vertex are either negatively charged (-0.1 e) or neutral, which indicates that the atoms at the base of the cluster transfer charge to the surface while the metal atoms at low coordinate sites, i.e. vertex and corners, accumulate electron density (Roldan et al. 2009). Thus, the Ni located at the vertex of the cluster could be a source of electrons for an eventual reaction with electron receptor molecules approaching the cluster from the gas phase (Tafreshi, Roldan & de Leeuw 2015). Analysing the electron density difference between the cluster and the surface (Figure 4-8), we have confirmed a charge accumulation only between the Ni atoms directly bonded to the surface and the surface atoms; there is no charge relocation between the top Ni atom which remains fully metallic. We also note the well-localised orbitals of the O$_6$ atoms interacting with the cluster. Eicher et al. has also shown this electron rearrangement between Pt clusters and the zirconia surface (Eichler 2005).
Figure 4-8. Calculated electron density difference between Ni$_n$ clusters and the surface for the most stable configuration of the Ni$_n$/ZrO$_2$(111) systems. Colour key: red, grey, and blue spheres correspond to oxygen, Zr and Ni atoms, respectively.

We have next analysed the interaction of Ni$_7$, Ni$_8$, Ni$_9$ and Ni$_{10}$ with the ZrO$_2$(111) surface where we have tried five, six, three and four non-equivalent initial configurations, respectively (Appendix-Figure 8-7 to Figure 8-10). The most stable shapes are shown in Figure 4-7 and the calculated clustering energies are 1.47, 1.42, 1.39 and 1.31 eV, respectively (Table 4-2). The four configurations have a similar pyramid shape and the only difference is the number of the Ni atoms at the top Ni layer of each cluster (Figure 4-7).
4.6.2 Ni\textsubscript{n}/YSZ(111) (n=1-10)

In the YSZ system, we have again built several clusters with non-equivalent initial adsorption configurations, both three-dimensional and flat, and adsorbed them on top of the YSZ(111) surface. A single Ni atom on top of the YSZ(111) surface sits on top of the oxygen vacancy as far as possible away from the yttrium atom with a clustering energy of 2.35 eV (Cadi-Essadek et al. 2015).

We have optimised several initial configurations for the flat Ni\textsubscript{2}/YSZ(111) and Ni\textsubscript{3}/YSZ(111) clusters (Appendix-Figure 8-11 and Figure 8-12) and the most stable ones are shown in Figure 4-9 with an average clustering energy of 2.21 eV (Table 4-2).
Figure 4-9. Side views of the most stable configurations of Ni$_n$/YSZ(111) systems. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.

For Ni$_n$ (n=4-7), the average $E_{clus}$ is 1.76 eV and the clusters adopt a Ni(111) facet shape, in agreement with a previous study by Li et. al. (J. Li et al. 2013) who showed that the Ni$_4$ cluster prefers to adopt a pyramid shape on top of $\gamma$-Al$_2$O$_3$, i.e. a similar
shape as found here. Similarly, Carrasco et al. (Carrasco et al. 2013) have also found that the pyramid Ni$_4$ geometry is preferred over the planar one, when the cluster is adsorbed on the isostructural CeO$_2$(111) surface.

In the Ni$_n$/YSZ(111) (n=2-7) configurations, the Ni-surface atomic spacing is 2.3 Å, i.e. slightly larger than in the ZrO$_2$(111) systems. In addition, each O$_u$ is pushed towards the neighbouring vacancy, since we observe an average decrease of 0.1 Å of the O$_u$-vacancy distance. This movement explains the preference of the Ni clusters to adsorb on this site: it is easier to drive the O$_u$ towards a vacancy where it tends to fill this defect. Moreover, the most stable adsorption site is the one involving two O$_u$ with one neighbouring oxygen vacancy.

Charge analysis (Table 4-2) shows a slight charge transfer from the cluster to the surface of ~ +0.2 e. As was observed for the Ni$_n$/ZrO$_2$(111) systems, this charge transfer affects the electronic structure of the surface: the charges of Zr and Y atoms (near the metal cluster) decrease from 2.2 to 2.1 e and the negative charge of O$_u$ decreases from -1.2 to -1.1 e. We also observe a charge accumulation on the Ni atom at the vertex of the pyramid of the Ni$_n$/YSZ(111) (n=4-7) configurations, since this latter atom has a -0.1 e charge. The electron density difference plot (Figure 4-10) shows this charge accumulation between the cluster and the surface and shows the localized orbitals of O$_u$ and Y atoms interacting with the cluster.
Figure 4-10. Calculated electron density difference for the most stable configuration of the Ni$_n$/YSZ(111) systems. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.

The flat shapes of the Ni$_n$/YSZ(111) (n = 2-7) structures, shown in the Appendix-Figure 8-11 to Figure 8-20, are less stable by ~0.11 eV, i.e. the Ni atoms prefer to
aggregate rather than spread over the surface, as was also observed for the Ni$_8$/ZrO$_2$(111) systems.

It is worth noting that for the Ni$_8$/YSZ(111) cluster, the flat and pyramid shapes are in equilibrium since their clustering energies differ by only 0.01 eV (Table 4-2). These two configurations are also the lowest energy ones from the six configurations considered (Appendix-Figure 8-21 to Figure 8-22). In the flat configuration (Appendix-Figure 8-21) the Ni$_8$ cluster interacts with six O$_u$ at an average Ni-O$_u$ distance of 2.0 Å. In addition, the oxygen vacancy is filled by one displaced O$_u$ which contributes to the stability of the system. Indeed, the movement of O$_u$ towards the vacancy allows the cluster to optimise its interaction with the other six O$_u$ surface atoms. This could be a drawback, for example in SOFC, since the role of the oxygen vacancies is to enhance the oxygen transport. As to the three-dimensional shape (Figure 4-9), the cluster interacts with five O$_u$ but none of the oxygen vacancies is filled by an O$_u$ atom. This shape is similar to the one found for Ni$_7$/YSZ(111), although the next Ni atom avoids interaction with Y from the surface and forms a (111)-facetted shape with the rest of the cluster. Bader charge analysis (Table 4-2) shows that the charge transfer from the cluster to the surface is slightly higher in the flat configuration (+0.3 e) than in the pyramid shape (+0.2 e) owing to the former’s interaction with an extra O$_u$ atom.

This comparison shows the importance of the two parameters responsible of the stability of the cluster on top of the surface: the number of the O$_u$ atoms interacting with the cluster and the shape of the cluster.
The last cluster studied in this work is Ni$_{10}$/YSZ(111), where three configurations have been considered (Appendix-Figure 8-25 and Figure 8-26), and the most stable shape found is the pyramid one (Figure 4-9). The calculated clustering energy is 1.58 eV (Table 4-2) which is similar to the value found for Ni$_{9}$/YSZ(111). This is predictable since both Ni$_{9}$/YSZ(111) and Ni$_{10}$/YSZ(111) have exactly the same shape and the only difference is the tenth Ni atom located at the apex of the pyramid in Ni$_{10}$/YSZ(111). Therefore the modification of the surface geometry upon adsorption and the number of O$_u$ involved in the interaction are similar to Ni$_{9}$/YSZ(111). As to the Bader charge (Table 4-2), the cluster is +0.3 e charged and we note that the Ni atom located at the apex of the cluster is -0.2 e charged, while all the other Ni are positively charged (average of +0.1 e). We also note the same variation of charge of the surface atoms interacting with Ni$_{10}$ as was observed for Ni$_{9}$/YSZ(111). Thus, the Ni atoms close to the surface transfer charge to the surface atoms and the Ni atom located at the top of the cluster, which can be seen from the electron density difference plot (Figure 4-10) where we have a gain of charge between the cluster and the surface.

In general, in Ni$_n$/YSZ(111) (n = 2-10), the Ni$_n$ clusters interact with O$_u$ with an average distance of 1.9 Å. The metal clusters transfer charge to the surface, depending on the size, ranging from +0.1 to +0.3 e. The three-dimensional cluster shape is more favourable due to the repulsive interaction between Y and Ni.
4.7 Ni\textsubscript{n}/ZrO\textsubscript{2}(111) (n=6-10) and Ni\textsubscript{n}/YSZ(111) (n=1-10): Ni sintering

We have shown that Ni\textsubscript{n} clusters on both ZrO\textsubscript{2}(111) and YSZ(111) surfaces prefer to adopt a three-dimensional structure rather than flat shapes for clusters containing at least 4 atoms. The same conclusion was drawn for a similar system, i.e. CeO\textsubscript{2}-supported Au nanoparticles (Kim et al. 2012), where it was shown that planar Au\textsubscript{13} on top of the CeO\textsubscript{2} surface is unstable compared to three-dimensional Au\textsubscript{13}. Pan et. al. (Pan et al. 2010) have also shown that a Ni\textsubscript{4} cluster prefers to adopt a 3-D pyramid shape on top of the γ-Al\textsubscript{2}O\textsubscript{3}(110) surface, with a large clustering energy. Giordano et al. (Giordano et al. 2001) have also demonstrated than the Ni\textsubscript{4} cluster prefers to adopt a tetrahedron shape on top of the MgO(001) surface.

The total energies of four individual Ni atoms (4Ni) compared to the Ni\textsubscript{4} cluster adsorbed on the surface are 3.38 eV and 2.20 eV less stable, respectively, on the ZrO\textsubscript{2}(111) and YSZ(111) surfaces, thus showing that aggregating of the Ni atoms is clearly preferred energetically over dispersion. We have also compared the total energy of two Ni\textsubscript{4} clusters, separated by approximately 6.0 Å, with the Ni\textsubscript{8}/surface system and here we also found that (N\textsubscript{i}+Ni\textsubscript{4}) is less stable than Ni\textsubscript{8}, now by 1.67 eV and 1.11 eV on ZrO\textsubscript{2}(111) and YSZ(111), respectively.

Furthermore, in Figure 4-11 (a) we have plotted the clustering energy (\textit{E}_{clus}) as a function of the cluster size, for both ZrO\textsubscript{2}(111) and YSZ(111) surfaces. This graph shows a probable aggregation of Ni on both surfaces owing to a thermodynamic driving force with increase of the cluster size. The trend of the clustering energy shows that for the same cluster size, the clustering energy is lower on ZrO\textsubscript{2}(111), in agreement with the two aggregation examples calculated for Ni\textsubscript{4} and Ni\textsubscript{8} clusters. The
Y atoms affect the geometry of the surface and anion rearrangement, making the interaction between the clusters and the O$_6$ surface atoms less favourable, thus enhancing the preference for the formation of Ni clusters.

We have also evaluated the difference between the cohesive energy ($E_{\text{coh}}$) and the clustering energy ($E_{\text{clus}}$) as a function of the cluster size. The difference between those energies expresses the trend to form a Ni-Ni bond instead of a Ni-surface bond. **Figure 4-11 (b)** shows that for both surfaces this energy difference decreases with increasing cluster size due to the preference of the Ni-Ni interaction over Ni-surface interactions. The $E_{\text{coh}} - E_{\text{clus}}$ graph also shows that for the same cluster size, the energy difference is lower for YSZ(111) than for ZrO$_2$(111), indicating that the ratio of interaction between Ni atoms is greater for Ni$_n$ clusters on top of YSZ(111).

The interaction energy ($E_{\text{int}}$) calculated as a function of the cluster size (**Figure 4-11 (c)**) confirms the affinity of the Ni$_n$ clusters for the ZrO$_2$(111) surface over YSZ(111). Note that the Ni cluster interaction energy is more favourable for zirconia than yttria-stabilized zirconia, which preference is even more striking for larger clusters. This demonstrates that cluster aggregation is more favourable on the YSZ(111) surface than on ZrO$_2$(111), in good agreement with, for instance, the difference in energy between two Ni$_4$ clusters and a Ni$_8$ cluster, which is larger for ZrO$_2$(111) than YSZ(111).
Figure 4-11. Plot of the clustering energy ($E_{clus}$), the difference between the clustering and cohesive energy ($E_{coh} - E_{clus}$) and the interaction energy ($E_{int}$) as a function of the cluster size on top of both ZrO$_2$(111) and YSZ(111) surfaces.
Chapter 4: Ni sintering on ZrO$_2$ and YSZ surfaces

Figure 4-12. Energy profile showing two transition states: from state (Ni+Ni$_4$)/YSZ(111) to Ni$_5$/YSZ(111) and from state (Ni+Ni$_{10}$)/YSZ(111) to Ni$_{10}$/YSZ(111). Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.

From Figure 4-12 we note that the Ni$_5$/YSZ(111) configuration is more stable than (Ni+Ni$_4$)/YSZ(111), indicating that Ni atoms prefer to aggregate to form larger clusters rather than wetting the surface. This is in good agreement with the graph in Figure 4-11, where we have shown a decrease of the $E_{coh} - E_{clus}$ difference, indicating the energetic favourability of aggregation of Ni atoms over their dispersion on both surfaces. From Figure 4-12 we also observe that the activation energy, i.e. the energy difference between the (Ni+Ni$_4$)/YSZ(111) structure and the transition state, is
\[ \Delta E_{Ni/YSZ} = 0.46 \text{ eV} \], which is lower than the same Ni collection adsorbed on ZrO\(_2\)(111) \((\Delta E_{Ni/ZrO_2} = 0.72 \text{ eV})\) (section 4.3). This difference in activation energies for the addition of a Ni to a larger cluster implies that single Ni atoms can more easily join a bigger cluster when those metal atoms are adsorbed on the YSZ(111) surface rather than ZrO\(_2\)(111), indicating that the aggregation of Ni atoms to form larger clusters, is facilitated when the zirconia surface is doped with yttria, again in good agreement with our \(E_{clus}\) and \(E_{coh} - E_{clus}\) plots in Figure 4-11. From \(E_{coh} - E_{clus}\) we also note that the activation energy between the \((Ni+Ni_{10})/YSZ(111)\) structure and the transition state \((\Delta E_{Ni_{10}/YSZ} = 0.035 \text{ eV})\) is approximately ten times lower than \(\Delta E_{Ni_{5}/YSZ} = 0.46 \text{ eV}\), indicating that the diffusion of Ni atoms towards bigger clusters is more favourable than towards smaller ones.

From the calculated activation energies, we can evaluate the hopping rate of one Ni atom from state \((Ni+Ni_n)/YSZ(111)\) to state \(Ni_{(n+1)}/YSZ(111)\): \(k_{A \rightarrow B}\) where A is either state \((Ni+Ni_4)/YSZ(111)\) or \((Ni+Ni_{10})/YSZ(111)\) and B is either state \(Ni_5/YSZ(111)\) or \(Ni_{10}/YSZ(111)\) (Figure 4-13). We have therefore calculated \(k_{A \rightarrow B}\) for a range of temperatures corresponding to the working temperature of the SOFC (T = 500°C-900°C). From Figure 4-13 we note that \(k_{A \rightarrow B}\) (for five Ni on the surface) varies from 1.05 \times 10^8 to 1.09 \times 10^{10} \text{ s}^{-1} which is higher than the values found for ZrO\(_2\)(111) \((k_{A \rightarrow B} \text{ varies from } 1.87 \times 10^7 \text{ to } 7.66 \times 10^8 \text{ s}^{-1})\) (section 4.4) indicating that the diffusion of a Ni atom towards a cluster is more favourable on the YSZ(111) surface. We also observe that the hopping rate is even higher when the cluster diffuses towards a larger
cluster, since for eleven Ni $k_{A\rightarrow B}$ varies from $586.99 \times 10^7$ to $703.93 \times 10^8 \text{ s}^{-1}$ (Figure 4-13). Thus, this evaluation of the hopping rate further strengthens the conclusions drawn from Figure 4-11: the aggregation of Ni atoms is preferred over dispersion on the surface and this aggregation is more favourable on the YSZ(111) surface.

Figure 4-13. Hopping rate for a Ni atom on YSZ(111).
4.8 Chapter conclusions

The general trend observed for Ni\textsubscript{n} clusters (n=2-10) adsorbed on the ZrO\textsubscript{2}(111) and YSZ(111) surfaces shows the importance of the interaction of Ni with the O\textsubscript{u} atoms as well as the shapes of the adsorbed Ni\textsubscript{n} clusters. We have seen that the O\textsubscript{u} atoms facilitate the adsorption of the clusters and that these atoms are shifted from their initial position upon adsorption. In Ni\textsubscript{n}/YSZ(111) systems, the clusters pushed the O\textsubscript{u} atoms towards filling neighbouring vacancies which could be a drawback in, for instance, SOFC since these vacancies play an important role in oxygen transport. Bader charge analysis of the clusters revealed that there is charge transfer from the cluster to the surface. Finally, the distribution of the charge within the cluster is similar for all clusters with a pyramid shape (Ni\textsubscript{n}, n=4-10), where the Ni atoms bound to the surface are positively charged and those at the top of the pyramid are either charge-neutral or indeed some negative charge is accumulated at the apex. In some instances, the Ni atoms located at the top of the clusters have a non-negligible amount of charge, which could play a role in the adsorption of molecules at the Triple Phase Boundary of the Ni/YSZ cermet: for example, an electrophile molecule would adsorb on top of the Ni cluster, rather than at the meeting point between the cluster and the surface. Finally, from calculation of the clustering and cohesive energies and evaluation of the diffusion barriers and hopping rates, we conclude that, on both ZrO\textsubscript{2}(111) and YSZ(111) surfaces, the sintering of the Ni atoms takes place spontaneously, especially on the YSZ(111) surface. A potential solution to clustering of the Ni particles may be the introduction of a dopant in order to trap the diffusing Ni atoms. We could also consider a reconstruction of the zirconia surface, as shown in the study by Tosoni et
al. (Tosoni et al. 2015), where the authors showed that the adsorption of Ru on a step on the ZrO$_2$ surface is more stable than on a regular surface.
Chapter 5

Adsorptions of molecules on Ni/ZrO$_2$ and Ni/YSZ interfaces

Abstract

In the solid oxide fuel cells (SOFC), the key reactions take place at the triple phase boundary (TPB), where molecules such as H$_2$O, CO$_2$ and CO interact and react. In this chapter, we have systematically studied the interaction of H$_2$O, CO$_2$ and CO with the dominant surfaces of four materials that are relevant to SOFC, i.e. ZrO$_2$(111), Ni/ZrO$_2$(111), YSZ(111) and Ni/YSZ(111) of cubic ZrO$_2$ stabilized with 9% of yttria (Y$_2$O$_3$). The study employed spin polarized density functional theory (DFT), taking into account the long-range dispersion forces. We have investigated up to five initial adsorption sites for the three molecules and have identified the geometries and electronic structures of the most stable adsorption configurations. We have also analysed the vibrational modes of the three molecules in the gas phase and compared them with the adsorbed molecules. A decrease of the wavenumbers of the vibrational modes for the three adsorbed molecules was observed, confirming the influence of the surface on the molecules’ intra-molecular bonds. These results are in line with the important role of Ni in this system, in particular for the CO adsorption and activation.
Chapter 5: Molecules adsorptions on Ni/ZrO$_2$ and Ni/YSZ interfaces

5.1 Introduction

As stated in the introduction of the thesis, both Ni/YSZ interaction and the reactions occurring at this interface lie at the core of the performance of the solid oxide fuel cell (SOFC) anode. In chapter 3 and 4 we focused on the interaction between Ni atoms and both ZrO$_2$(111) and YSZ(111) surfaces. The next step is to study the interaction between these metal-oxide interfaces and molecules involved in the reactions in the SOFC such as H$_2$O, CO$_2$ and CO which is the aim of this chapter.

One of the species used as fuel in the SOFC are H$_2$ and CO which are oxidized at the anode of the SOFC (Hanna et al. 2014). Electrochemical oxidation of H$_2$ is a multistep process where adsorption, surface reactions and charge transfer are observed during the reaction (Sukeshini et al. 2006). The reaction at the anode is described by equation (5-1) (Atkinson et al. 2004):

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (5-1)$$

In the CO oxidation on Ni/YSZ, CO adsorbs associatively on Ni and then diffuses towards the triple phase boundary (TPB), where the gas phase, Ni particles and YSZ surface meet. Here, it is oxidized by O$^{2-}$ coming from the electrolyte i.e. the solid oxide (equation (5-2) (Lauvstad et al. 2002)):

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (5-2)$$

Instead of pure H$_2$ or CO, H$_2$/CO mixtures can be used leading to more complicated mechanisms since other reactions than direct oxidations are involved such as water-gas shifting (Hanna et al. 2014) (equation (5-3)) (Novosel et al. 2008; Yoshio Matsuzaki & Yasuda 2000; Andreassi et al. 2009).
Chapter 5: Molecules adsorptions on Ni/ZrO\textsubscript{2} and Ni/YSZ interfaces

\[ CO + H_2O \rightarrow CO_2 + H_2 \] \hspace{1cm} (5-3)

All these molecules interact with the supported Ni and the surface, thus necessitating the study of these molecules in contact with the TPB, which plays a key role in the performance of the SOFC (Hauch, Bowen, et al. 2008). In the past few years many researchers have investigated the microstructure and the chemistry of the TPB. For example, Liu et al. (Liu & Jiao 2005) have shown experimentally that impurities such as SiO\textsubscript{2} can degrade the Ni/YSZ grain boundaries, whereas Jensen et al. (Jensen et al. 2001) have shown that impurities segregate from the bulk of the YSZ material and accumulate along the TPB.

Several \textit{ab initio} investigations have been carried out on the interaction of molecules with the Ni/YSZ cermet (Shishkin & Ziegler 2010; Cucinotta et al. 2011; Ammal & Heyden 2012; Shishkin & Ziegler 2009). Shishkin et al. (Shishkin & Ziegler 2010) showed the oxidation of hydrogen at the TPB by the oxygen atoms bound to Zr (or Y) and Ni. Cucinotta et al. (Cucinotta et al. 2011) showed that the hydrogen oxidation can be active away from the TPB, when water is adsorbed on the oxide surface. Ammal et al. (Ammal & Heyden 2012) combined DFT and microkinetic studies to show that the O migration pathway is faster than the H spillover and OH migration pathway. Shishkin and Ziegler (Shishkin & Ziegler 2009) have studied the oxidation of H\textsubscript{2}, CH\textsubscript{4} and CO at the Ni/YSZ interface and showed that the YSZ cermet is inert to fuel oxidation, while Ni is active towards fuel adsorption and oxidation. However, a systematic characterization of H\textsubscript{2}O, CO\textsubscript{2} and CO molecules at the TPB is still missing. We have therefore investigated the interaction of these three molecules on
four relevant surfaces, i.e. ZrO$_2$(111), Ni/ZrO$_2$(111), YSZ(111) and Ni/YSZ(111), and compared our results with experimental data.

We have investigated up to five initial adsorption sites for each molecule on the pristine surfaces (ZrO$_2$(111) and YSZ(111)) and two more on the surfaces with supported Ni (Ni/ZrO$_2$(111) and Ni/YSZ(111)). We have elucidated the geometries and electronic structures of the most stable adsorption sites and compared these results with other reported computational models, where available, and supported our findings by experimental and computational infrared spectra (IR).

5.2 Model and Computational Methods

All the structural relaxations and frequency calculations have been performed using the Vienna Ab-initio Simulation Package (VASP) (Kresse & Furthmüller 1996b; Kresse & Furthmüller 1996a; Kresse & Hafner 1993; Kresse & Hafner 1994), solving the Kohn-Sham equations of the density functional theory (DFT) (Hohenberg & Kohn 1964) in a periodic approximation. The calculations have been carried out adopting the generalized gradient approximation (GGA) (Perdew et al. 1996) with the Perdew-Burke-Ernzerhof (PBE) density functional. The semi-empirical method of Grimme (Grimme 2006) was employed to describe and improve the long-range dispersion interactions. The H (1 s), C (2 s, 2 p), O (2 s, 2 p), Ni (3 d, 4 s), Zr (4 d, 5 s) and Y (4 s 4p 4 d 5 s) atomic orbitals have been treated as valence electrons, while the remaining electrons were considered as core electrons and kept frozen. To describe the interaction between the valence and the core electrons, we adopted the projected
augmented wave method (PAW) (P E Blöchl 1994). The plane-waves kinetic energy cutoff was fixed at 500 eV, and all the calculations were spin-polarized. The conjugate gradient technique has been used for the geometry optimizations with an interatomic force threshold of 0.01 eV/Å. Monkhorst-Pack grids with a 7x7x1 k-point mesh were used to sample the reciprocal space for the 1x1 slab calculations. For the molecules in the gas phase a 1x1x1 mesh of k-points was used and each molecule was positioned in a large box (14x15x16 Å³) in order to avoid lateral interactions. The rest of the settings were similar to those used for the slab calculations.

The procedure to compute the vibrational frequencies is implemented in the VASP software. The vibrational frequencies were evaluated by finite displacements of every coordinate and the vibrational frequencies thus correspond to the eigenvalues of the diagonal Hessian matrix (second derivative of the energy with respect to the atomic positions), where the eigenvectors are the vibrational normal modes of the system. Frequency changes reflect a structural modification of the molecules upon adsorption on the surfaces.

To describe the (111) surfaces we have used the same slab model as the one discussed in chapter 3 where we set up a perpendicular vacuum size of 15 Å, i.e. large enough to avoid interactions with its periodic images. Following previous results exposed in chapter 3 the surfaces were O-terminated and contained 9 atomic layers (three O-Zr-O trilayers); the 5 top atomic layers were allowed to relax fully during geometry optimization, while the 4 layers at the bottom were kept fixed, thereby simulating the bulk material. The surface area is 44.96 Å².
The four surfaces (ZrO$_2$(111), Ni/ZrO$_2$(111), YSZ(111) and Ni/YSZ(111)) were taken from our previous work exposed in chapter 3. There, we had substituted two Zr (from the topmost and the sub-surface O-Zr-O trilayers) by Y with the removal of one oxygen from the third atomic layer (the next nearest neighbour of Y atoms) to obtain the YSZ(111) surface (Zr$_{10}$Y$_2$O$_{23}$(111) slab) (yttria = 9.1 wt%). Then, Ni was deposited on the most favourable adsorption site on both the ZrO$_2$(111) and YSZ(111) surfaces. On the ZrO$_2$(111) surface, Ni sits preferentially on the O$_{d-}$ atom, i.e. slightly off from the perpendicular, Figure 5-1, while on the YSZ(111) it adsorbs preferentially on top of the oxygen vacancy and away from the Y atoms (Figure 5-1).

The magnetization of the Ni atom before adsorption was 0.57 $\mu$B (Ni atom from bulk calculation). Upon adsorption on both ZrO$_2$(111) and YSZ(111) surfaces, the calculated magnetisation for the adsorbed Ni atom was 0.0 $\mu$B (singlet configuration). For comparison, we have also forced the Ni atom to be in a triplet configuration (2.0 $\mu$B) and the calculated total energies were 1.16 and 1.44 eV higher for Ni/ZrO$_2$(111) and Ni/YSZ(111), respectively, than the values found for the singlet configuration. Moreover, a study made by Hahn et al. (Hahn et al. 2015) took into account different spin states of Ni$_{10}$ cluster adsorbed on CeO$_2$(111) surface and they showed that the singlet configuration of the cluster is stable, as it is only 0.01 eV higher in energy than the configuration where the multiplicity is 11.

The three molecules (H$_2$O, CO and CO$_2$) were initially positioned at 2.0 Å above the surface and different orientations have been compared for each initial adsorption site. On the ZrO$_2$(111) surfaces, four initial adsorption sites were tested for each molecule:
on top of the Zr atom, above the outermost oxygen $O_u$ (up) or $O_d$ (down), and finally at the centre of the $O_u$-$O_d$-$Zr$ “triangle”, see Figure 5-1. On the YSZ(111) surface, six initial adsorption sites were investigated: the Zr atom, the outermost oxygen $O_u$ (up), $O_d$ (down), the oxygen vacancy, the yttrium atom, and the centre of the $O_u$-$O_d$-$Zr$ “triangle”, see Figure 5-1. For each initial adsorption site, we have relaxed the molecules, as well as the five top layers of the slab (as described in the previous paragraph). On the Ni/ZrO$_2$(111) and Ni/YSZ(111) surfaces, we identified two initial adsorption sites: near the Ni atom and approximately over the most stable adsorption site found for the naked surface. The non-equivalent initial adsorption sites leading to unstable configurations are presented in the annexe. We have calculated the binding energy, taking into account the zero point energy (ZPE), as the difference between the energy of the slab with the molecule adsorbed ($E_{molecule/surface}$) and the sum of the energies of the clean oxide surface ($E_{surface}$) and the isolated molecule ($E_{molecule}$), equation (5-4).

$$E_B = E_{molecule/surface} - (E_{surface} + E_{molecule})$$

(5-4)

We have also calculated the Van der Waals binding energies as the difference between the estimated Van der Waals energy of the slab with the molecule adsorbed ($E_{vdW/molecule/surface}$) and the sum of the estimated Van der Waals energies of the clean oxide surface ($E_{vdW/surface}$) and the isolated molecule ($E_{vdW/molecule}$), equation (5-5).

$$E_{vdW_B} = E_{vdW/molecule/surface} - (E_{vdW/surface} + E_{vdW/molecule})$$

(5-5)

We have analysed the charge transfer between the surface and the molecules using Bader analysis as implemented in the Henkelman algorithm (Bader 1991). To evaluate
the interaction between the molecules and the surface atoms we have also calculated the electron localization function (ELF) which measures the probability of finding an electron in the neighbourhood of another electron with the same spin (Becke & Edgecombe 1990).

**Figure 5-1.** Side and top views of the O-terminated ZrO$_2$(111), YSZ(111), Ni/ZrO$_2$(111) and Ni/YSZ(111) surfaces. Red, grey, blue and cyan spheres represent oxygen, zirconium, nickel, and yttrium atoms, respectively. The oxygen vacancy is represented by the yellow sphere.
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5.3 Results and discussion

5.3.1 Structural analysis and electronic structure

5.3.1.1 ZrO₂(111)

The evaluation of the binding energies for the three molecules shows that the strength of their adsorption on the ZrO₂(111) surface follows the trend: H₂O > CO > CO₂ (see Table 5-1). H₂O is likely to be dissociated, where one H is transferred to a surface oxygen with the OH remaining on top of the Zr atom (Figure 5-2). The dissociative water adsorption on ZrO₂ was also observed in a previous investigation by Korhonen et al. (Korhonen et al. 2008), where they showed experimentally and theoretically that water, at low coverage, dissociates on the monoclinic zirconia surface. Our calculated binding energy for [H+OH]-ZrO₂(111) (-1.08 eV) is similar to the adsorption on their monoclinic (111) and the (101) zirconia surfaces (-1.20 eV). The most stable adsorption site found for CO₂ and CO molecules is on top of the zirconium atom (Figure 5-2). The binding energy for CO₂ on ZrO₂(111) (-0.24 eV) is close to a previous study (-0.26 eV) (Hornebecq et al. 2011), where the authors had modelled the zirconia surface by four types of clusters and saturated the dangling bonds with hydrogen atoms: Zr₂O₁₄H₂₀, Zr₃O₁₆H₂₀, Zr₃O₁₉H₂₆ and Zr₅O₂₄H₂₈ (Appendix-Figure 8-31). The Zr₂O₁₄H₂₀ and Zr₃O₁₉H₂₆ exhibit OH groups, while in Zr₃O₁₆H₂₀ and Zr₅O₂₄H₂₈ only H atoms are adsorbed on the oxygen clusters. The main difference between Zr₃O₁₆H₂₀ and Zr₅O₂₄H₂₈ is the Zr atom pointing outwards from the Zr₅O₂₄H₂₈ cluster. For Zr₅O₁₆H₂₀ the calculated CO₂ binding energy was -0.26 eV (similar to this work) and the authors (Hornebecq et al. 2011) showed that CO₂ is physisorbed at 2.70
Å away from the cluster and adopting a parallel position, comparable to our geometry (Figure 5-2). On top of the Zr$_2$O$_{14}$H$_{20}$ and Zr$_3$O$_{19}$H$_{26}$ clusters, the authors (Hornebecq et al. 2011) found a stronger CO$_2$ binding energy (-0.34 and -0.35 eV, respectively), but CO$_2$ is still physisorbed since for both clusters the CO$_2$-cluster distance remains larger than 2.10 Å, indicating that the OH groups play a minor role in the CO$_2$ adsorption. On top of Zr$_5$O$_{24}$H$_{28}$ the CO$_2$ adsorption was much stronger (-0.67 eV) but the authors showed, using the multi-Langmuir model, that the Zr$_5$O$_{24}$H$_{28}$ site is less abundant than the three other sites. Thus, at high CO$_2$ loading, the authors (Hornebecq et al. 2011) concluded that CO$_2$ adsorbs onto the Zr$_2$O$_{14}$H$_{20}$, Zr$_3$O$_{16}$H$_{20}$ and Zr$_3$O$_{19}$H$_{26}$ clusters. In our study, the most stable adsorption found for CO on ZrO$_2$(111) is stronger (-0.37 eV) than the one on O$_4$ suggested by Walter et al. (Walter et al. 2001) (-0.14 eV), which in our model was evaluated to be -0.10 eV.
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Table 5-1. Calculated binding energies per molecule ($E_B$ in eV) and charges (q in e) for the 3 molecules (H$_2$O, CO$_2$ and CO) adsorbed on the most favourable site of the 4 surfaces: ZrO$_2$(111), Ni/ZrO$_2$(111), YSZ(111) and Ni/YSZ(111).

<table>
<thead>
<tr>
<th></th>
<th>ZrO$_2$(111)</th>
<th>Ni/ZrO$_2$(111)</th>
<th>YSZ(111)</th>
<th>Ni/YSZ(111)</th>
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<tr>
<td>$E_B$(H$_2$O)</td>
<td>--</td>
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<td>$E_B$(H+OH)</td>
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<td>-1.33</td>
<td>-0.30</td>
<td>-0.52</td>
</tr>
<tr>
<td>$E_B$(CO$_2$)</td>
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<td>-1.35</td>
<td>-0.36</td>
<td>-0.31</td>
</tr>
<tr>
<td>$E_B$(CO)</td>
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<td>-0.37</td>
<td>-2.32</td>
</tr>
<tr>
<td>q(H$_2$O)</td>
<td>--</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
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<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>q(CO$_2$)</td>
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<td>-0.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>q(CO)</td>
<td>0.0</td>
<td>-0.2</td>
<td>0.0</td>
<td>-0.3</td>
</tr>
</tbody>
</table>

Among the three molecules, dissociated H$_2$O has a stronger affinity for the ZrO$_2$(111) surface than CO$_2$ and CO. The variation of the interatomic distances is in good agreement with the binding energies and the transferred charges (Table 5-1). For instance, [H+OH] is the closest species to the ZrO$_2$(111) surface. Figure 5-2 shows that O (of OH) is at 2.070 Å over the top zirconium atomic layer, while the closest atom, O for CO$_2$ and C for CO, are positioned at 3.009 Å and 2.500 Å, respectively, from the surface which, added to a lack of charge transfer, suggests that both molecules are physisorbed.
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5.3.1.1.2 Ni/ZrO$_2$(111)

On the Ni/ZrO$_2$(111) surface, the strength of adsorption of the molecules near Ni is as follow: CO > H$_2$O > CO$_2$.

Table 5-1 shows that, depending on the activation energies, H$_2$O dissociation is practically in equilibrium with molecular adsorption since $E_B$(H$_2$O)-Ni/ZrO$_2$(111) ~ $E_B$[H+OH]-Ni/ZrO$_2$(111) (-1.39 and -1.33 eV respectively). The binding energy of CO$_2$ (-1.35 eV) is similar to H$_2$O but considerably weaker than the one found for CO (-2.70 eV), which will surround the single atom, replacing both CO$_2$ and H$_2$O.

There is no obvious change in the H$_2$O intra-molecular bond distances. However, the intra-molecular CO$_2$ bond length increases from 1.2 Å (gas phase) to 1.3 Å (CO$_2$-Ni/ZrO$_2$(111)) and the CO bond length increases from 1.1 Å to 1.2 Å (CO-
A previous study also reported these elongations of the intra-molecular distances upon interaction of the molecules with supported metal cluster on oxide surfaces (Briquet et al. 2010). Meanwhile, H₂O remains practically unaltered, whereas CO₂ and CO indicate an electronic rearrangement which is not seen on the bare ZrO₂(111). Charge analysis shows a gain of charge for CO₂ (-0.5 e) and CO (-0.2 e) upon adsorption on the Ni/ZrO₂(111). The outermost Zr atomic layer and the Ni atom lose +0.3 e and +0.2 e, respectively, while for CO-Ni/ZrO₂(111) only the outermost Zr atomic layer transfers +0.2 e, through the Ni adatom, to the CO molecule.

The electron localization function (ELF) plots in Figure 5-3 show the effect of the Ni on the molecules’ adsorption onto the surface. In the H₂O-Ni/ZrO₂(111) case, the electron localization is negligible between H and the oxygen belonging to the surface, whereas the electrons localized on the oxygen atom of the water molecule interact favourably with the empty orbitals of the Ni atom, showing that Ni facilitates the adsorption of H₂O on the Ni/ZrO₂(111) surface. In Figure 5-3 we note a bonding region between CO₂ and Ni, which is not observed in the CO₂-ZrO₂(111) system. This interaction explains the strengthening of the CO₂ adsorption over Ni/ZrO₂(111) compared to the bare ZrO₂(111) surface. The shape of the ELF around the carbon atom from CO changes in the presence of Ni: it points towards the Ni atom, showing the important effect of the metal atom.

In Figure 5-4 we show the total density of states (DOS) of the three molecules (H₂O, CO₂ and CO) adsorbed on ZrO₂(111) and Ni/ZrO₂(111) and the projected DOS on the three relevant atoms (C, O and H) and the Ni atom. A sharp peak (specific orbital)
means that a specific orbital is located at this specific energy. Thus, when many orbitals of different atoms have the same energy (well localized) we consider that the interaction between those orbital atoms are favourable. On the other hand, the interaction is unfavourable if the peaks of the different orbital atoms are spread over a range of energies (delocalized).

We have shown, in the [H+OH]/ZrO$_2$(111) density of states (DOS) (Figure 5-4), that the peaks located below the Fermi energy correspond to the s and p orbitals of OH oxygen and are delocalized. However, in the H$_2$O-Ni/ZrO$_2$(111) system, they are localized and positioned at the same energy as the final two Ni s p d orbital peaks (-0.26, -0.20 and -0.01 eV). This favours the interaction between the Ni atom and the H$_2$O oxygen orbitals which is in good agreement with the ELF analysis.

Similar situations occur with the CO$_2$ and CO molecules, i.e. their orbitals below the Fermi energy are dispersed over a range of energies when interacting with a naked surface, but are localized peaks in the presence of Ni atoms. The peaks at these energies correspond to Ni, O and C orbitals, indicating that an interaction exists between the molecule and Ni/ZrO$_2$(111) and that this interaction is facilitated by the Ni atom, which confirms the ELF analysis discussed above.
Figure 5-3. Electron localization function (ELF) of the three molecules (H$_2$O, CO$_2$ and CO) adsorbed on top of the 4 surfaces: ZrO$_2$(111), Ni/ZrO$_2$(111), YSZ(111) and Ni/YSZ(111). A high ELF value along the bond path reflects a strong interaction between the molecule and the surface while a low ELF value is the consequence of a weak interaction.
Figure 5-4. Total density of states (DOS) of the three molecules (H$_2$O, CO$_2$ and CO) adsorbed on ZrO$_2$(111) and Ni/ZrO$_2$(111) and projected DOS on the three molecule atoms (C, O and H) and Ni atom. We represent here both spin up ($\alpha$) and down ($\beta$) of the total DOS and the spin up for the projected DOS. Colour scheme is labelled in the inset. H$_{\text{vac}}$ and H$_{\text{surf}}$ correspond to H pointing towards the vacuum and the surface, respectively. The oxygen pointing towards the vacuum and the surface are represented by O$_{\text{vac}}$ and O$_{\text{surf}}$, respectively. To facilitate the reading of the graphs, we have multiplied the intensity of the PDOS where necessary (multiplication factor shown in parentheses).
We have shown that the adsorption of the molecules on ZrO$_2$(111) and Ni/ZrO$_2$(111) can lead to the dissociation of H$_2$O, and causes the elongation of the intramolecular bonds of CO and CO$_2$. In addition, the ELF plot indicates the significant effect of Ni on the electronic structure of the molecules, thereby enhancing their chemisorption. These results are in agreement with previous investigations, which have shown that metal particles can stabilize the adsorption of the molecule on the surface (Molina et al. 2004; Chen et al. 2007; Duan & Henkelman 2015; J. Li et al. 2013). For example, Carrasco et al. (Carrasco et al. 2013) showed that CO prefers to bind to the Ni$_3$/CeO$_2$(111) surface, rather than on the pristine CeO$_2$(111) surface, in a similar configuration as the one presented in Figure 5-2.

5.3.1.1.3 YSZ(111)

We have followed the same procedure on the ~ 9% yttria-doped ZrO$_2$(111). The binding energies of these molecules on the YSZ(111) shows the following preference for binding: H$_2$O > CO > CO$_2$ (Table 5-1).

Unlike the water adsorption on ZrO$_2$(111), H$_2$O prefers to remain as a molecule on YSZ(111) since $E_B$(H$_2$O)-YSZ(111) is more favourable than $E_B$(H+OH)-YSZ(111) by ~ 0.5 eV (Table 5-1). The CO$_2$ adsorption becomes ~ 0.1 eV stronger compared with the pristine ZrO$_2$(111). Both H$_2$O and CO$_2$ adsorb near the yttrium atom in a slightly tilted position, whereas CO binds perpendicularly to the surface (Figure 5-2). The CO binding energy is -0.37 eV, i.e. very close to the one on ZrO$_2$(111) and in good agreement with the DFT study by Yurkiv et al. (-0.34 eV) (Yurkiv et al. 2012).
The analysis of the interatomic distances from the structures in Figure 5-2 agrees with the trend in binding energies, since H₂O is stabilized by H bonds with the surface (H-O₆surf = 1.744 Å), and CO₂ and CO are not strongly bound. There is negligible variation in the intra-molecular distances or charge transfer for any of the three molecules. The electronic structure and the charge transfer compared with the pristine ZrO₂(111) indicate that the interaction of CO₂ and CO molecules is barely modified by the presence of Y-dopants. However, H₂O prefers to adsorb molecularly on the YSZ(111) surface, whereas it dissociates upon adsorption on the ZrO₂(111) surface.

5.3.1.1.4 Ni/YSZ

Once Ni is deposited on YSZ(111), the trend in the adsorption of the molecules changes from the naked surface and the preference becomes: CO > H₂O > CO₂. As on YSZ(111), H₂O adsorbs molecularly on Ni/YSZ(111), although the difference in binding energy compared to the dissociated configuration is only 0.15 eV, indicating a close thermodynamic equilibrium (depending on the energy barrier to dissociation). H₂O adsorbs near the Y and away from Ni, while CO₂ and CO prefer to adsorb near the Ni atom with binding energies of -0.31 and -2.32 eV respectively. Only CO has more affinity for the Ni/YSZ(111) surface than for YSZ(111), releasing almost 2 eV more than on the bare YSZ(111) surface. Thus, as a general trend, H₂O and CO₂ adsorb on the bare surface, while CO is strongly attached to Ni/YSZ(111) (Table 5-1).
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The distance analysis of the structures in Figure 5-2 shows that H$_2$O and CO$_2$ are at approximately 2.0 Å from the surface, while the C atom (of CO) is 1.696 Å from the Ni atom. There is no obvious increase in either H$_2$O or CO$_2$ intra-molecular bond lengths. However, the CO bond increases by 0.1 Å upon adsorption, in agreement with the strong adsorption and the charge transfer of -0.3 e from the outermost zirconium atomic layer. As such, Ni acts as an electrode, which is its main function in SOFC: electrons are transferred from the surface through Ni. The other molecules remain neutral upon adsorption.

To investigate further the role of Ni, we have compared the ELF for the YSZ(111) and Ni/YSZ(111) systems. Figure 5-3 shows that the perturbation of the ELF upon adsorption of H$_2$O and CO$_2$ is negligible, which agrees with physisorption and the insignificant effect of Ni. However, the perturbation of the electrons surrounding the CO molecule is considerable in the presence of Ni.

In the H$_2$O-Ni/YSZ(111) DOS (Figure 5-5) we observe five localized peaks (-0.89, -0.85, -0.67, -0.12 and -0.04 eV) below the Fermi level, corresponding to the Ni s p d orbitals. The contribution of the H$_2$O orbitals to these peaks is negligible, indicating that H$_2$O interacts weakly with both YSZ(111) and Ni/YSZ(111) surfaces, in good agreement with the low binding energies and the ELF analysis. The conclusion is similar for the CO$_2$/YSZ(111) and CO$_2$-Ni/YSZ(111) systems, where the DOS plots show that the CO$_2$ orbitals do not contribute to the valence band, in agreement with the weak adsorption and the ELF plots. However, the presence of Ni causes the CO orbitals to be localized at the same energy as the Ni orbitals below the Fermi level (
0.72, -0.62, and -0.48 eV), leading to a stronger interaction. Thus, Ni stabilizes CO adsorption on the Ni/YSZ(111) surface, as was also observed from the ELF analysis.
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Figure 5-5. Total density of states (DOS) of the three molecules (H$_2$O, CO$_2$ and CO) adsorbed on YSZ(111) and Ni/YSZ(111) surfaces and projected DOS on the three molecule atoms (C, O and H) and Ni atom. We represent here both spin up (α) and down (β) of the total DOS and the spin up for the projected DOS. Colour scheme is labelled in the inset. To facilitate the reading of the graphs, we have multiplied the intensity of the PDOS where necessary (multiplication factor shown in parentheses).
5.3.1.2 Infrared spectra

We have calculated and analysed the IR spectra of the three molecules in the gas phase and compared them with the molecules adsorbed on the four surfaces (Figure 5-6), which provides data that are directly comparable with simple experimental characterization, thus providing circumstantial evidence of the geometries and electronic structures described above.

For example, the molecularly adsorbed water is confirmed by the presence of a bending mode around 1600 cm\(^{-1}\), since there is no OH-related vibrational mode at 1600 cm\(^{-1}\) (Henderson 2002). Similarly, analysing the IR spectra of adsorbed CO\(_2\) and CO indicates a potential dissociative chemisorption of CO\(_2\), as was shown by previous studies where CO\(_2\) is adsorbed on top of silica-supported iron (Freund & Roberts 1996). In Table 5-2 we show the IR spectra values related to Figure 5-6 and compare them with the experimental values from the literature (Shimanouchi n.d.; Coblentz Society n.d.).

5.3.1.2.1 ZrO\(_2\)(111) and Ni/ZrO\(_2\)(111)

The wavenumbers of the vibrational modes of the water molecule drop upon adsorption on both the ZrO\(_2\)(111) and Ni/ZrO\(_2\)(111) surfaces. A drop of the bending mode is observed (\(\Delta \delta_{H_2O-ZrO_2(111)} = 474 \text{ cm}^{-1}\)) upon H\(_2O\) adsorption on the ZrO\(_2\)(111) surface compared to the gas phase, but since H\(_2O\) adsorption is dissociative on ZrO\(_2\)(111) the bending mode observed in [H+OH]-ZrO\(_2\)(111) actually corresponds to the bending mode of both hydrogens: the H transferred to the surface and the H bonded to O\(_{\text{water}}\). This frequency variation of the bending mode was expected, since upon
adsorption the H-O\textsubscript{water} and H-O\textsubscript{surf} bonds are weaker than the H-O bonds in the water molecule in vacuum. Similarly to [H+OH]-ZrO\textsubscript{2}(111), there are two different stretching modes, one each corresponding to ν(H-O\textsubscript{surf}) and ν(H-O\textsubscript{water}). In addition, Table 5-2 shows, that from these stretching modes ν(H-O\textsubscript{surf}) has the lowest wavenumber, which is predictable since the H-O\textsubscript{surf} bond is weaker than H-O\textsubscript{water}. The wavenumber of the two stretching modes of H\textsubscript{2}O over Ni/ZrO\textsubscript{2}(111) are even lower than the ones found for ZrO\textsubscript{2}(111). This is in good agreement with the larger binding energy of H\textsubscript{2}O-Ni/ZrO\textsubscript{2}(111): H\textsubscript{2}O binds more strongly to Ni/ZrO\textsubscript{2}(111) than ZrO\textsubscript{2}(111), which weakens its internal bonding by electronic rearrangement, thus explaining the decrease of the stretching modes of H\textsubscript{2}O-Ni/ZrO\textsubscript{2}(111).
Figure 5-6. Theoretical IR spectra of the free and adsorbed molecules (H$_2$O, CO$_2$ and CO) on ZrO$_2$(111), Ni/ZrO$_2$(111), YSZ(111) and Ni/YSZ(111). Inset in parenthesis are the infra-red experimental values from the literature.
Table 5.2. Theoretical vibrational frequencies (ω) in cm\(^{-1}\) for H\(_2\)O, CO\(_2\) and CO in the gas phase and adsorbed on the 4 surfaces (ZrO\(_2\)(111), Ni/ZrO\(_2\)(111), YSZ(111) and Ni/YSZ(111)). ν, ν\(_s\), ν\(_\text{as}\), and δ denote stretching, symmetrical stretching, asymmetrical stretching and bending modes, respectively.

We show in parenthesis the infra-red experimental values from the literature.

<table>
<thead>
<tr>
<th></th>
<th>H(_2)O assignment</th>
<th>H(_2)O ω</th>
<th>CO(_2) assignment</th>
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The adsorption of CO\(_2\) is weak on ZrO\(_2\)(111), with the wavenumbers of the three different vibrational modes remaining similar to the gas phase (Table 5.2). However, it adsorbs strongly on Ni/ZrO\(_2\)(111), lowering the wavenumbers of the asymmetrical and symmetrical stretching modes by 571 and 148 cm\(^{-1}\), respectively. Indeed, the stronger adsorption of CO\(_2\) on top of Ni/ZrO\(_2\)(111) affects the strength of the CO\(_2\) bonds, which explains the drop of the wavenumbers of the stretching modes observed in CO\(_2\)-Ni/ZrO\(_2\)(111). The bending mode of CO\(_2\)-Ni/ZrO\(_2\)(111) increases by 103 cm\(^{-1}\) compared to CO\(_2\)-ZrO\(_2\)(111). The reason for this increase is explained by the rearrangement of the electronic structure of CO\(_2\) upon adsorption on Ni/ZrO\(_2\)(111).
where CO$_2$ gains a charge of 0.5 e. As to CO, the difference in stretching mode upon adsorption on ZrO$_2$(111) is negligible compared with the gas phase: $\Delta \nu_{\text{CO-ZrO}_2(111)} = -3$ cm$^{-1}$, confirming the physisorbed state, which is in good agreement with the experimental study made by Dulaurent et al. (Dulaurent & Bianchi 2001) ($\nu$(CO) = 2185 cm$^{-1}$). On Ni/ZrO$_2$(111), the wavenumber of the stretching mode is even lower ($\Delta \nu_{\text{CO-Ni/ZrO}_2(111)} = 131$ cm$^{-1}$), in good agreement with the strong binding energy and increase of the C-O distance.

5.3.1.2.2 YSZ(111) and Ni/YSZ(111)

Vibrational modes of H$_2$O on YSZ(111) and Ni/YSZ(111) show a decrease in wavenumbers compared to the gas phase, although they remain higher than on ZrO$_2$(111). The asymmetrical and symmetrical stretching and bending modes of H$_2$O are located at lower wavenumber, when it is adsorbed on YSZ(111) and on Ni/YSZ(111) (Table 5-2). This analysis agrees with the weakness of the intramolecular bonds on both doped surfaces, as described before.

CO$_2$ adsorbs on both YSZ(111) and Ni/YSZ(111) surfaces, leading to a decrease in the wavenumber of each vibrational mode (Table 5-2). These shifts of the vibrational modes upon adsorption are related to the decreased strength of CO$_2$ bonds due to the interaction with the surfaces and the occupation of the molecular antibonding orbitals leading to a bent structure. Our calculated value for the symmetrical stretching mode of CO$_2$ on YSZ(111) (1317 cm$^{-1}$) is in the same range as the experimental study made by Köck et al. (Köck et al. 2013), who found a peak of a bridged carbonate at 1305
The binding energies of CO-YSZ(111) and CO-Ni/YSZ(111) agree with the CO affinity for these two surfaces. For example, on Ni/YSZ(111) the stretching mode of the CO molecule is observed at significant lower wavenumber than in the gas phase (Table 5-2), having decreased by 135 cm\(^{-1}\). The increase in the length of the CO bond upon adsorption and its weakening further shows the strong interaction between CO and the bare and Ni-decorated YSZ surfaces.

To summarize the general trend of the vibrational modes of the molecules upon adsorption, we have plotted in Figure 5-7 the variation of the stretching modes as a function of the binding energies.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure57.png}
\caption{Plot of the variation of the symmetric (\(\nu_s\)) and asymmetric (\(\nu_{as}\)) stretching modes upon adsorption. ●, ■, ▲ and ♦ represent ZrO\(_2\)(111), Ni/ZrO\(_2\)(111), YSZ(111) and Ni/YSZ(111) surfaces, respectively. \(E_B\) corresponds to the total binding energy. Since H\(_2\)O adsorbs dissociatively on ZrO\(_2\)(111) the variation of H\(_2\)O stretching mode on ZrO\(_2\)(111) is not represented here. \(\nu_{as}\) is not represented for CO as in the gas phase CO has one stretching mode.}
\end{figure}

Note that the H\(_2\)O dissociation is not represented here. We have observed that, when the molecules adsorb weakly onto the surface, the shift in the wavenumber of the
Chapter 5: Molecules adsorptions on Ni/ZrO$_2$ and Ni/YSZ interfaces

stretching mode is negligible and the molecule-surface interaction is mainly due to van der Waals interactions. In Table 5-3 we compare $E_B$ with $(E_B - E_B^{vdW})$, where $E_B$ and $E_B^{vdW}$ correspond to the total and Van der Waals binding energies, respectively. We observe from Table 5-3 that for the weak adsorptions, such as CO$_2$-ZrO$_2$(111) and CO$_2$-Ni/YSZ(111), $(E_B - E_B^{vdW})$ is approximately equal to zero, indicating that the molecule-surface interaction arises mainly from the Van der Waals interactions. For other systems, such as H$_2$O-Ni/YSZ(111), CO$_2$-YSZ(111) and CO-ZrO$_2$(111), the contribution of the Van der Waals interactions is still non-negligible since $(E_B - E_B^{vdW})$ is approximately twice as high as $E_B$.

For the strong interactions (H$_2$O-Ni/ZrO$_2$(111), CO$_2$-Ni/ZrO$_2$(111), CO-Ni/ZrO$_2$(111) and CO-Ni/YSZ(111)), the shift of the stretching mode is considerable (Figure 5-7) and the contribution of the Van der Waals interactions is negligible, since the negative value of $(E_B - E_B^{vdW})$ is lower than -1 eV (Table 5-3).

Table 5-3. Calculated $E_B$ and $(E_B - E_B^{vdW})$ in eV for the 3 molecules (H$_2$O, CO$_2$ and CO) adsorbed on the most favourable site of the 4 surfaces: ZrO$_2$(111), Ni/ZrO$_2$(111), YSZ(111) and Ni/YSZ(111). $E_B$ and $E_B^{vdW}$ correspond to the total and Van der Waals binding energies, respectively.

<table>
<thead>
<tr>
<th></th>
<th>H$_2$O</th>
<th>CO$_2$</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_B$</td>
<td>$E_B - E_B^{vdW}$</td>
<td>$E_B$</td>
</tr>
<tr>
<td>ZrO$_2$(111)</td>
<td>--</td>
<td>-0.24</td>
<td>-0.01</td>
</tr>
<tr>
<td>Ni/ZrO$_2$(111)</td>
<td>-1.39</td>
<td>-1.21</td>
<td>-1.35</td>
</tr>
<tr>
<td>YSZ(111)</td>
<td>-0.82</td>
<td>-0.68</td>
<td>-0.36</td>
</tr>
<tr>
<td>Ni/YSZ(111)</td>
<td>-0.67</td>
<td>-0.52</td>
<td>-0.31</td>
</tr>
</tbody>
</table>
5.4 Chapter conclusions

We have studied systematically the interaction of H$_2$O, CO$_2$ and CO on the naked and Ni-decorated ZrO$_2$(111) and YSZ(111) surfaces, where we have employed DFT with long-range interaction corrections to characterize the bonding character of these molecule-metal-support interfaces. We found that thermodynamically H$_2$O adsorbs dissociatively on ZrO$_2$(111), but in the presence of Ni both dissociated and molecular H$_2$O can coexist. On the other hand, molecular water is likely to be present on YSZ(111) and Ni/YSZ(111), depending on the experimental conditions. Regardless of which surface is considered, the charge transfer is negligible upon H$_2$O adsorption, except for the dissociated state. CO$_2$ shows very weak adsorption on the surfaces studied with the exception of Ni/ZrO$_2$(111), where the molecule is activated by the transfer of 0.5 e. Here, the metal is slightly more oxidized leading to a decrease in the stretching modes of CO$_2$. The CO adsorption depends strongly on the presence of Ni at the surface; on the Ni-decorated surfaces, CO adsorbs more strongly than H$_2$O and CO$_2$, while on the naked surfaces CO binds mainly by long-distance interactions. The interatomic distance analysis agrees with the trend in binding energies, since on Ni-decorated surfaces the CO-surface distance is smaller than both H$_2$O-surface and CO$_2$-surface distances. Thus, it appears that the role of Ni at the TPB is to provide electrons to CO with a subsequent shift in the IR spectrum. We have also explored the relationship between the binding energy and the variation in the stretching modes where we noted a negligible shift in the wavenumber of the stretching mode for the molecules interacting weakly with the surface.
Clearly, the incorporation of a single nickel atom is an approximate model for the triple-phase boundary, and our results may change if the metal-oxide systems were to include finite nickel clusters or even nanoparticles. In the next chapter, we will therefore investigate how Ni clusters of increasing sizes affect the interaction of the metal clusters with the gaseous molecules.
Chapter 6

**CO$_2$ Adsorption on Ni$_n$/YSZ(111) Interfaces**

**Abstract**

In this chapter we have investigated the interaction of a CO$_2$ molecule with the clean YSZ(111) surface and with Ni$_n$/YSZ(111) (n =1, 4-7, 10, 20) interfaces, using spin polarized density functional theory (DFT) and also considering long-range dispersion forces. We have considered up to six initial adsorption sites and two orientations for the CO$_2$ molecule, which showed that the adsorption is stronger on the Ni$_n$/YSZ(111) (n =4-7, 10, 20) interface than on the clean YSZ(111) and Ni$_1$/YSZ(111) systems. Additionally, we have determined that the preferential adsorption site of CO$_2$ is at the interface between the Ni$_n$ (n =4-7, 10, 20) cluster and the YSZ(111) surface, where we have observed a bending and stretching of the molecule, demonstrating activation of the CO$_2$ molecule upon adsorption. The CO$_2$-Ni$_n$/YSZ(111) interaction is due to a charge transfer between the metal cluster and the molecule and a mixing between Ni orbitals and CO$_2$ orbitals. We show that, although the electronic structure of the clusters depends on the cluster size, the interaction strength of CO$_2$ with the interface is independent of the size of the supported nickel particle. We have also evaluated the
Chapter 6: CO$_2$ adsorption on Ni$_x$/YSZ(111) interfaces

reverse water gas shift reaction on Ni$_x$/YSZ(111) where we have determined one hydrocarboxylic intermediate and two transition states
6.1 Introduction

Significant effort is expended on the identification of a catalytic system, which is capable of converting CO$_2$ to liquid fuels, where the activation of CO$_2$ is a key step in the conversion (Pan et al. 2009). For instance, co-electrolysis of CO$_2$ and H$_2$O could be used in solid oxide fuel cells (SOFCs) to recycle CO$_2$ into sustainable hydrocarbon fuels (Jensen et al. 2007; Ebbesen & Mogensen 2009; Graves, Ebbesen & Mogensen 2011; Hartvigsen et al. 2008; Yang et al. 2015; Zhan et al. 2009; Fu et al. 2010; Hauch, Ebbesen, et al. 2008). During the cell operation both CO$_2$ and H$_2$O are supplied to the anode of the fuel cell (Graves, Ebbesen & Mogensen 2011) where they interact with the catalyst. Following other authors who have used density functional theory (DFT) calculations to study the interaction of CO$_2$ with metal-oxide interfaces (Hahn et al. 2013; Hahn et al. 2015), we have used DFT to focus on the interaction of CO$_2$ with different cluster sizes of nickel supported on yttria-stabilized zirconia (YSZ).

Several DFT studies have focused on the adsorption and activation of CO$_2$ on other metal-oxides systems (Liu et al. 2015; Zhang et al. 2011), such as M$_2$/$\gamma$-Al$_2$O$_3$ (M = Sc-Cu) which showed a charge transfer from the oxide-supported metal to the CO$_2$ molecule leading to the adsorption and bending of CO$_2$ (Pan et al. 2009). Pan et al. (Pan et al. 2010) studied the CO$_2$ hydrogenation on Ni/$\gamma$-Al$_2$O$_3$. They adsorbed separately CO$_2$ and H adatoms on supported Ni$_4$ clusters before describing the co-adsorption of both molecules. On the clean Ni$_4$/$\gamma$-Al$_2$O$_3$ they found that CO$_2$ interacts with two Ni atoms via its C atom and both O atoms, where the molecule is activated as shown by the bending and elongation of C-O bonds upon adsorption. They have
also explored the elementary steps in the CO$_2$ conversion, typically to formate and carboxyl groups, on both dry and hydrogenated Ni/$\gamma$-Al$_2$O$_3$ surfaces. They showed that on the clean surface the formation of formate is kinetically feasible, while the pathway leading to CO is thermodynamically more favourable. However, on the hydroxylated surface, the CO formation is preferred both kinetically and thermodynamically.

Another CO$_2$ hydrogenation study on Cu/ZnO(0001) (Yang et al. 2010) confirmed the importance of the supported metal cluster in the reaction mechanism: the authors showed at theoretical level that the reaction is faster on supported Cu clusters than on the Cu(111) surface, owing to low coordinated-Cu sites that contribute to the stabilization of the reaction intermediates. Similarly, Vidal et al. (Vidal et al. 2012) showed that CO$_2$ activation is more favourable on Cu/TiC than on the Cu(111) surface. The adsorption of CO$_2$ over Cu-Co supported on $\gamma$-Al$_2$O$_3$ showed a CO$_2$ activation upon adsorption, where the hydroxylated surface stabilized the adsorbed CO$_2$ by either hydrogen bonding or protonating CO$_2$ (Yin et al. 2011). Tang et al. (Tang et al. 2009) used first principles kinetic Monte Carlo simulations to study CO$_2$ hydrogenation on the Cu/ZrO$_2$ interface. In their investigation, the authors firstly described the interaction of CO$_2$ with Cu/ZrO$_2$, where they showed that CO$_2$ prefers to adsorb on the naked ZrO$_2$ surface, rather than at the Cu/ZrO$_2$ interface. They calculated a binding energy of 0.69 eV and also described the bending of the molecule upon adsorption. They also noted a stretching of the C-O bonds and charge transfer from the ZrO$_2$ surface to the antibonding $2\pi_{\mu}$ orbital of CO$_2$. 

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Despite these studies, a systematic investigation of the influence of the size of supported metal clusters on the CO$_2$ adsorption is still lacking. Here, we have studied the interaction of seven systems (YSZ(111) and Ni$_n$/YSZ(111) (n =1, 4-7, 10, and 20)) with a CO$_2$ molecule and we have analysed the geometric structure and the vibrational frequencies to describe the configuration of the adsorbed molecule at the interface. We have also characterized the electronic structure to evaluate the charge transfer between the interfacial systems and the CO$_2$ molecule. Finally, we have investigated the reverse water gas shift reaction which is the reaction between the adsorbed CO$_2$ molecule and H$_2$ generating water and carbon monoxide.

### 6.2 Model and computational methods

Similarly to previous chapters, to model the most stable cubic zirconia surface, the ZrO$_2$(111) O-terminated surface (Grau-crespo et al. 2007; Cadi-Essadek et al. 2015), we cleaved the c-ZrO$_2$ bulk using the METADISE code (Watson et al. 1996) and placed it in a slab model. Thus, in this chapter, the ZrO$_2$(111) slab contains 9 atomic layers (three O-Zr-O trilayers), where the 5 top atomic layers were relaxed during geometry optimisation and the 4 layers in the bottom were kept fixed to represent the bulk crystal. The YSZ(111) surface was built by the substitution of two Zr (from the top and the sub O-Zr-O trilayers) by two Y (9.1 w% of yttria) with the removal of one oxygen from the third atomic layer (the next nearest neighbour of Y atoms). Side and top views of ZrO$_2$(111) and YSZ(111) are shown in Figure 6-1. The location of the Y dopants and oxygen vacancy were determined in previous chapters.
Figure 6.1. (a) and (b) describe the side and top view, respectively, of the oxygen-terminated ZrO$_2$(111) surface. (c) and (d) show the side and top view, respectively, of the YSZ(111) surface.

Color key: O, Zr and Y are respectively represented by a red, grey and cyan sphere. The yellow sphere corresponds to the oxygen vacancy.

We have repeated the unit cell in the x and y surface directions to avoid lateral interactions between the Ni$_n$ clusters. Thus, our YSZ(111) surface is modelled by a Zr$_{40}$Y$_8$O$_{92}$(111) slab. We discussed in chapter 4 all the non-equivalent geometries and initial adsorption sites for the Ni$_n$ clusters, which showed that the most stable configuration for the clusters is a pyramid shape, rather than a flat shape on top of the
YSZ(111) surface. Additionally, we observed that the Ni\textsubscript{n} clusters adsorb away from the Y atoms. Figure 6-2 shows the most stable Ni\textsubscript{n}/YSZ(111) \((n=1, 4-7, 10, 20)\) configurations on which we have adsorbed the CO\textsubscript{2} molecule, where the average size of the Ni\textsubscript{n} clusters ranges from 3.63 Å\(^2\) \((n = 4)\) to 41.10 Å\(^2\) \((n = 20)\).

Figure 6-2. Stable configurations of Ni\textsubscript{n} \((n = 1, 4-7, 10, 20)\) clusters adsorbed on the YSZ(111) surface. Color key: O, Zr, Y and Ni are respectively represented by red, grey, cyan and blue spheres. The yellow sphere corresponds to the oxygen vacancy.
The calculations in this study are based on spin-polarized Density Functional Theory (DFT) and performed by solving the Kohn-Sham equations (Hohenberg & Kohn 1964) in a periodic system as implemented in the Vienna Ab-initio Simulation Package (VASP) (Kresse & Furthmüller 1996b; Kresse & Furthmüller 1996a; Kresse & Hafner 1993; Kresse & Hafner 1994). Exchange-correlation potentials are modelled by the general gradient approximation (GGA) (Perdew et al. 1996) using the Perdew-Burke-Ernzerhof (PBE) density functional. The long-range dispersion interactions were described by the semiempirical method of Grimme (Grimme 2006), which showed an improvement in the description of the molecular adsorption (Dzade et al. 2015; Tafreshi, Roldan & De Leeuw 2015; Haider et al. 2014). The C (2 s, 2 p), O(2 s, 2 p), Ni (3 d, 4 s), Zr (4 d, 5 s) and Y (4 s 4p 4 d 5 s) electrons have been treated explicitly as valence states, while the inner electrons were considered as core electrons and kept frozen. The core-valence electron interaction has been treated with the projected augmented wave method (PAW) (P E Blöchl 1994). A plane-wave kinetic energy cutoff of 500 eV has been chosen. Geometry optimisation has been performed using the conjugate gradient technique with an interatomic force threshold of 0.01 eV/Å and the transition states were located with the dimer method (Heyden et al. 2005). Monkhorst-Pack grids of 3x3x1 k-point sampling were used for the 2x2 slab calculations. The gas phase CO$_2$ molecule was placed in a large box (14x15x16 Å$^3$) in order to avoid lateral interactions using 1x1x1 k-point sampling.

The vibrational frequencies of CO$_2$ (in the gas phase and adsorbed on the surface) were calculated by finite displacements of every coordinate, where the eigenvalues of the Hessian matrix correspond to the vibrational normal modes. CO$_2$ frequency
changes, upon adsorption, reflect an alteration of interatomic bonds, where, for example, a shift towards higher frequency values indicates stronger bonds.

### 6.3 Results and discussion

**6.3.1 Geometric structure**

We have evaluated the interaction of CO\textsubscript{2} with both the bare YSZ(111) and Ni\textsubscript{n}/YSZ(111) surfaces and have calculated the binding energy of CO\textsubscript{2} (\(E_B\)) on the surfaces as follows (equation (6-1)):

\[
E_B = E_{\text{CO}_2-\text{surface}} - (E_{\text{surface}} + E_{\text{CO}_2})
\]

Where \(E_{\text{CO}_2-\text{surface}}\) is the energy of the YSZ(111) surface (with or without the Ni\textsubscript{n} cluster) and the adsorbed CO\textsubscript{2}. \(E_{\text{surface}}\) and \(E_{\text{CO}_2}\) are the energies of the surface system without CO\textsubscript{2} and the CO\textsubscript{2} molecule in the gas phase, respectively. A positive binding energy reflects an endothermic CO\textsubscript{2} adsorption on Ni\textsubscript{n}/YSZ(111), while a negative binding energy means an exothermic CO\textsubscript{2} adsorption and therefore a favourable interaction between CO\textsubscript{2} and the Ni\textsubscript{n}/YSZ(111) interface.

We have tried several initial adsorption sites for CO\textsubscript{2} on the clean YSZ(111) surface and on the supported Ni\textsubscript{n} clusters on YSZ(111). On Ni\textsubscript{n}/YSZ(111), CO\textsubscript{2} has been initially adsorbed on the top and edge of the Ni\textsubscript{n} cluster, at the interface between the Ni\textsubscript{n} cluster and the oxide surface, as well as away from the Ni\textsubscript{n} cluster. We have considered at least two CO\textsubscript{2} orientations for each initial adsorption site. Figure 6-3 represents the most stable adsorbed geometries.
On the clean surface, CO$_2$ prefers to adsorb near the Y atom with a binding energy of -0.37 eV (Table 6-1) and adopting a tilted position. Upon adsorption CO$_2$ remains linear with an angle between the molecule and the surface of 121.38°. The CO$_2$-surface distance is 2.688 Å and the average internal C-O bond is 1.177 Å which is similar to the C-O distance calculated for the gas phase molecule, indicating that the CO$_2$-surface interaction is weak. This CO$_2$-YSZ(111) interaction has been discussed in detail in chapter 5.
Table 6-1. Calculated binding energy ($E_{B}$, in eV), distances (in Å), OCO angle ($\theta_{\text{OCO}}$, in degrees) and charge (q, in e) of CO$_2$ adsorbed on YSZ(111) and Ni$_n$/YSZ(111) (n = 1, 4-7, 10, 20).

<table>
<thead>
<tr>
<th>Surface</th>
<th>$E_{B}$</th>
<th>CO internal bonds</th>
<th>CO$_2$-surf atom distance</th>
<th>CO$_2$-Ni$_n$ distance</th>
<th>$\theta_{\text{OCO}}$</th>
<th>Total charge before CO$_2$ adsorption</th>
<th>Total charge upon CO$_2$ adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ(111)</td>
<td>-0.37</td>
<td>1.183, 1.170</td>
<td>2.688</td>
<td>--</td>
<td>--</td>
<td>177.16</td>
<td>--</td>
</tr>
<tr>
<td>Ni$_4$/YSZ(111)</td>
<td>-0.32</td>
<td>1.181, 1.172</td>
<td>2.842</td>
<td>3.655</td>
<td>4.555</td>
<td>177.76</td>
<td>+0.3 +0.3 0.0</td>
</tr>
<tr>
<td>Ni$_{10}$/YSZ(111)</td>
<td>-1.16</td>
<td>1.253, 1.256</td>
<td>4.424</td>
<td>1.971</td>
<td>1.983, 2.075</td>
<td>2.065</td>
<td>137.94 +0.1 +0.7 -0.7</td>
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<td>Ni$_{10}$/YSZ(111)</td>
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<td>1.265, 1.274</td>
<td>2.303</td>
<td>1.884, 2.430</td>
<td>2.706, 2.019</td>
<td>128.92</td>
<td>+0.2 +0.8 -0.8</td>
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<tr>
<td>Ni$_{20}$/YSZ(111)</td>
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<td>127.47</td>
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</tr>
<tr>
<td>Ni$_{20}$/YSZ(111)</td>
<td>-1.24</td>
<td>1.263, 1.260</td>
<td>3.623</td>
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<td>136.15</td>
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</tr>
<tr>
<td>Ni$_{20}$/YSZ(111)</td>
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<td>1.247, 1.268</td>
<td>4.531</td>
<td>1.899, 2.141</td>
<td>2.230, 1.971</td>
<td>135.22</td>
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</tr>
<tr>
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<td>-1.49</td>
<td>1.265, 1.256</td>
<td>3.200</td>
<td>1.888, 2.108</td>
<td>2.091, 2.029</td>
<td>136.03</td>
<td>+0.2 +1.0 -0.7</td>
</tr>
</tbody>
</table>

In Figure 6-3, we observe that CO$_2$/YSZ(111) and CO$_2$-Ni$_1$/YSZ(111) have a similar geometry and comparable binding energies: -0.37 and -0.32 eV, respectively (Table 6-1). On Ni$_1$/YSZ(111), CO$_2$ adsorbs at a distance of 2.842 Å from the yttrium atom and the average internal C-O bond is 1.177 Å, the molecule also remains linear and is at an angle of 117.82$^\circ$ to the oxide surface. Thus, one Ni atom does not affect significantly the CO$_2$ adsorption properties of the YSZ(111) surface.

From Table 6-1 we note that for Ni$_n$ (n≥4) clusters supported on YSZ(111) $E_B$ is -1.16 eV, or larger which is approximately three times stronger than the binding energies found on either CO$_2$/YSZ(111) or CO$_2$-Ni$_1$/YSZ(111), indicating that the Ni$_n$ (n≥4) clusters stabilize the CO$_2$ adsorption. Our calculated binding energies for CO$_2$-Ni$_n$/YSZ(111) (n≥4) are in the same range as the one obtained by Pan et al. (Pan et al. 2010) (0.93 eV) in their study of CO$_2$ hydrogenation on Ni/γ-Al$_2$O$_3$. From Figure 6-3 we note that CO$_2$ adsorbs on the edge of the cluster, at the interface with the YSZ(111), indicating that CO$_2$ hydrogenation occurs on Ni$_n$/YSZ(111) (n≥4) with an activation energy of 0.93 eV.
where the C atom binds at least one Ni atom: the C-Ni distance calculated for Ni₉/YSZ(111) interfaces (n=4-7, 10, 20) ranges from 1.859 to 2.451 Å (Table 6-1).

The calculated C-Ni distances at the Niₙ/YSZ(111) interfaces (n=4-7, 10, 20), are comparable to the study by Hahn et al. (Hahn et al. 2015), where they found a C-Ni distance of 1.89 Å and showed that CO₂ adsorbs on top of Ni₁₀/CeO₂(111) with similar geometries to the ones presented in Figure 6-3.

We also note that CO₂ interacts with Niₙ clusters through its oxygen atoms (O¹ and O²) at distances ranging from 1.8-1.9 Å (Table 6-1). The YSZ(111) surface also plays a role in the CO₂ adsorption, since the CO₂ oxygen pointing towards the surface interacts with Zr atoms as shown in Figure 6-3. The O¹-surface distance varies depending on the cluster shape: for the geometries where the cluster is slightly tilted towards the surface, i.e. CO₂-Ni₅/YSZ(111) and CO₂-Ni₁₀/YSZ(111), the O¹-surface distance is shorter than the one found in the geometries where the cluster adopts a configuration parallel to the surface, i.e. CO₂-Ni₉/YSZ(111) (n = 4, 7, 10 and 20) (Table 6-1 and Figure 6-3).

In Figure 6-4 a) we have plotted the average of the difference between the internal C-O¹ and C-O² distances in the gas phase and after adsorption (Δd_{C-O} = (d_{C-O¹} - 1.177) + (d_{C-O²} - 1.177)/2, where 1.177 Å is the internal C-O distance in the gas phase) as a function of the binding energy. We have also plotted the molecule’s angle as a function of the binding energy (Figure 6-4 b)). The calculated values of C-O¹, C-O² and θ_{OCO} are shown in Table 6-1.
Figure 6-4. Elongation ($\Delta d_{c-o}$, in Å) and angle ($\theta_{OCO}$, in deg) of CO$_2$ adsorbed on YSZ(111) and Ni$_n$/YSZ(111) ($n = 1, 4-7, 10, 20$). Blue area indicates activated CO$_2$ molecule.
**Figure 6-4** clearly shows that the internal C-O bonds vary only weakly upon CO$_2$ adsorption on both YSZ(111) and Ni$_i$/YSZ(111) interfaces. However, on the Ni$_n$/YSZ(111) ($n = 4-7, 10, 20$) interfaces where CO$_2$ chemisorbs, the internal C-O elongation is more notable: $\Delta d_{c-o}$ ranges from 0.078 to 0.097 Å which is in good agreement with the strong CO$_2$ adsorption. Additionally, we have noted that the stretching of the C-O internal bonds is asymmetric as shown in Table 6-1: generally the C-O$^2$ (the one pointing towards the gas phase) is larger than C-O$^1$ distance, except on Ni$_7$/YSZ(111) and Ni$_{20}$/YSZ(111). This asymmetric stretching upon CO$_2$ adsorption on Ni$_n$/YSZ(111) interfaces suggests that O$^2$ would separate more easily than O$^1$ from the molecule, as was also suggested by Hahn et al. (Hahn et al. 2015).

This asymmetry provides insight into the mechanism of the CO$_2$ reduction in SOFC: the hydrogenation of O$^2$ may lead to CO + H$_2$O, yielding CH$_3$OH, while HCOOH is the product of the hydrogenation of O$^1$.

The CO$_2$ activation is confirmed by the O-C-O angle analysis (**Figure 6-4**). The CO$_2$ bending is more pronounced upon adsorption on supported clusters than on the clean YSZ(111) surface or supported single Ni atom. As expected, for the strongest adsorption we obtained the smallest angle (CO$_2$-Ni$_6$/YSZ(111)) and strongest bending. This CO$_2$ activation has also been observed on similar systems (Pan et al. 2009), where the authors showed that CO$_2$ prefers to adopt a bent geometry on top of its most favourable adsorption site: the interface between the oxide support ($\gamma$-Al$_2$O$_3$) and the transition metal dimer (Sc-Cu).
6.3.2 Frequency analysis

In Figure 6-5 we have plotted the infrared (IR) spectra of CO$_2$ adsorbed on pristine and Ni$_n$ decorated YSZ(111) surfaces and compared them with the IR spectra of CO$_2$ in the gas phase. The variation of the position of the peaks upon the molecule’s adsorption confirms the change in the CO$_2$ geometry and weakening of the intra-molecular bonds. We have also compared the IR spectra of the adsorbed molecule with experimental data to characterize the structures determined in this work and validate the geometries of the CO$_2$ adsorbed on the Ni$_n$/YSZ(111) interfaces.

Figure 6-5. Modelled IR spectra of CO$_2$ in the gas phase, on naked YSZ(111) and on CO$_2$-Ni$_n$/YSZ(111) (n = 1, 4-7, 10, 20). Inset in parenthesis are the infra-red experimental values from the literature (Shimanouchi n.d.).
In the gas phase, CO$_2$ has two calculated vibrational modes active in IR: the asymmetrical stretching ($\nu_{\text{as}} = 2378 \text{ cm}^{-1}$) and the bending ($\delta = 634 \text{ cm}^{-1}$) modes. As shown in Figure 6-5, our calculated values of CO$_2$ IR in the gas phase, are in good agreement with the experimental values from the literature (667 and 2349 cm$^{-1}$ for $\delta$ and $\nu_{\text{as}}$, respectively) (Shimanouchi n.d.).

Upon adsorption on YSZ(111) and Ni$_n$/YSZ(111) the average shift of the asymmetrical stretching is 20 cm$^{-1}$, which is in good agreement with the weak binding energy and small internal bond elongation of CO$_2$ upon adsorption. On Ni$_n$/YSZ(111) ($n = 4$-$7$, 10, 20) interfaces, where the CO$_2$ adsorbs more strongly than on YSZ(111) and Ni$_1$/YSZ(111), we note an average shift of 748 cm$^{-1}$ of the asymmetrical stretching mode. The reason for this decrease is the weakening of the CO$_2$ internal bond upon adsorption. This shift confirms the distance analysis, where we showed an increase of the C-O distances. Mudiyanselage et al. (Mudiyanselage et al. 2013) have studied the water-gas shift reaction (WGSR) on a similar system to this investigation, i.e. the CeO$_x$/Cu(111) interface. They showed experimentally and theoretically by DFT a 700 cm$^{-1}$ shift in $\nu_{\text{as}}$ upon CO$_2$ adsorption at the interface, which is in the same range as our value (748 cm$^{-1}$), confirming the similarities of the adsorption and activation of CO$_2$ on oxide/metal interfaces such as Ni$_n$/YSZ(111) ($n = 4$-$7$, 10, 20). Graciani et al. (Jesús Graciani, Kumudu Mudiyanselage, Fang Xu, Ashleigh E. Baber, Jaime Evans, Sanjaya D. Senanayake, Darío J. Stacchiola, Ping Liu, Jan Hrbek, Javier Fernández Sanz 2014) have also shown that the CeO$_x$/Cu(111) interface activates CO$_2$, as they observed experimentally two IR peaks at 1288 and 1610 cm$^{-1}$ corresponding to the presence of a carboxylate species (CO$_2$$\delta^-$) on the surface (Seiferth et al. 1999). These
values agree with our findings where $v_s$ and $v_{as}$ are at 1170 cm$^{-1}$ and 1630 cm$^{-1}$, respectively, on Ni$_n$/YSZ(111) (n = 4-7, 10, 20) interfaces.

Figure 6-5 also indicates that the symmetrical stretching ($v_s$) of adsorbed CO$_2$ becomes active in IR as a consequence of the dipole perpendicular to the surface, which increases once the molecule bends. In addition, the bending of the molecule leads to an increase in the value of the bending mode ($\delta$): the average calculated shift of $\delta$ is 79 cm$^{-1}$ upon adsorption at the Ni$_n$/YSZ(111) (n = 4-7, 10, 20) interfaces.

6.3.3 Electronic structure

In Table 6-1 we have shown the Bader charge analysis of the Ni$_n$ clusters before and after CO$_2$ adsorption. The average calculated charge for Ni$_n$ clusters supported on YSZ(111) is +0.2 e. However, the charge distribution within the cluster is not uniform: the Ni atoms located at the interface with the surface are positively charged (average of +0.1 e), while the Ni atoms at the top are negatively charged (average of -0.1 e). Once CO$_2$ adsorbs, the Ni atoms interacting with CO$_2$ lose an average charge of 0.3 e: the charge of the top Ni atom (Ni$^2$ - Figure 6-3) increases from -0.1 e to +0.2 e, while the charge of the bottom Ni atom (Ni$^1$ - Figure 6-3), directly interacting with CO$_2$, increases from +0.1 e to +0.4 e.

As to the CO$_2$ molecule, we have evaluated an average charge transfer of -0.8 e upon adsorption on Ni$_n$-YSZ(111) (n = 4-7, 10, 20), coming mainly from the Ni$_n$ clusters since the charge of the surface atoms neighbouring CO$_2$ remains unchanged. However, on Ni$_6$/YSZ(111), we have observed a slight charge transfer from a surface oxygen
atom to the CO\textsubscript{2} molecule; the surface O (interacting with CO\textsubscript{2} oxygen) increases by 0.1 e.

We have also characterized the adsorbed CO\textsubscript{2} species by plotting the electron density difference as \( \Delta \rho = \rho_{\text{CO}_2-\text{surface}} - (\rho_{\text{surface}} + \rho_{\text{CO}_2}) \) in Figure 6-6, which shows charge accumulation between the CO\textsubscript{2} oxygens and the cluster. The strong CO\textsubscript{2}-Ni\textsubscript{n}/YSZ(111) (n=4-7, 10, 20) interactions come mainly from C-Ni\textsubscript{n} bond formation, as shown by the accumulation of charge density between the C and the metal cluster. We have observed a polarization of the CO\textsubscript{2} oxygen atom by the surface oxygen and zirconium in CO\textsubscript{2}-Ni\textsubscript{n}/YSZ(111) (n= 5 and 6), since there is a depletion of charge.
between the CO$_2$ oxygen and the surface atoms and an accumulation of charge between the CO$_2$ oxygen and the surface. This is in good agreement with the charge transfer from the surface atom to the molecule discussed previously. The electron density difference analysis confirms our previous observation, i.e. that the CO$_2$-Ni$_n$/YSZ(111) ($n$=4-7, 10, 20) interaction is mainly due to the interaction of the CO$_2$ molecule with the Ni$_n$ cluster, whereas we have observed only a slight interaction between CO$_2$ and the YSZ(111) surface atoms.

**Figure 6-7.** Total density of states (DOS) of CO$_2$-Ni$_n$/YSZ(111) in grey and projected density of states on C of CO$_2$, O of CO$_2$, and Ni$_n$ clusters, in black, red and blue, respectively.
The representation of the projected density of states (PDOS) of CO$_2$-Ni$_n$/YSZ(111) (n = 4-7, 10 and 20) (Figure 6-7) reveals peaks in the band gap of the YSZ surface corresponding to d-type Ni orbitals. The number of the d-type orbitals in the band gap increases with the cluster size, as it has been shown previously where Ni$_n$ clusters have been adsorbed on the CeO$_2$ surface (Hahn et al. 2015). There is metal d mixing with the CO$_2$ orbitals, leading to bonding and antibonding states related to the bending of the molecule upon adsorption. This behaviour is in good agreement with the study by Choe et al. (Choe et al. 2000), where they investigated the adsorption of CO$_2$ on Pt(111) and Fe(111). They used the atom superposition and delocalization molecular orbital theory to show the relation of the bending of CO$_2$ on the surfaces with the mixing of the d metal orbitals and the CO$_2$ orbitals.

### 6.3.4 Reverse water gas shift reaction

We have studied the catalytic properties of the Ni/YSZ interface for the reverse water gas shift (RWGS) reaction (equation (6-2)) by proposing one of the possible reaction paths:

$$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad (6-2)$$

We have chosen to study the RWGS reaction for a small cluster size, i.e. Ni$_5$/YSZ(111). This model is accurate enough as we found that the CO$_2$ adsorption geometry is similar regardless of the Ni cluster size. The adsorbate binds at the edge of the cluster with minimal interaction with the YSZ surface.

We have tried several adsorption sites and orientations of the H$_2$ molecule and show in Figure 6-8 the most stable geometry of H$_2$-Ni$_5$/YSZ(111).
Figure 6-8. Representation of the most stable configurations of a) H$_2$, b) CO$_2$, and c) CO$_2$-H$_2$ on Ni$_3$/YSZ(111). The Bader charge of the adsorbed molecules are shown next to each configuration. Colour key: O, Zr, Y, Ni, C, and H are respectively represented by red, grey, cyan, blue, black, and white spheres. The yellow sphere corresponds to the oxygen vacancy.

From Figure 6-8 we note that H$_2$ adsorbs dissociatively on Ni$_3$/YSZ(111) and each hydrogen sits on the face of the pyramid Ni cluster. The dissociation of H$_2$ upon adsorption on Ni/YSZ observed in this investigation is in good agreement with previous studies (Cucinotta et al. 2011; Shishkin & Ziegler 2010). The calculated binding energy is -1.51 eV and we note a charge transfer from the Ni$_3$/YSZ(111) surface to both hydrogen atoms (Figure 6-8 a)). H$_2$ and CO$_2$ adsorb on Ni$_3$/YSZ(111) with a similar binding energy (Figure 6-8). However, we did not find competition of the adsorbates for the same adsorption sites. This led us to consider a geometry where hydrogen atoms are adsorbed on the faces of the metal cluster and the CO$_2$ molecule on its edge. Figure 6-8 c) corresponds to the most stable geometry of the (CO$_2$-H$_2$)-
Chapter 6: \( \text{CO}_2 \text{ adsorption on Ni}/\text{YSZ}(111) \text{ interfaces} \)

Ni\(_3\)/YSZ(111) system, which is the starting point of the RWGS reaction (equation (6-2)).

From our calculations, the first step of the RWGS reaction is the hydrogenation of the \( \text{CO}_2 \) molecule. One of the H can either go towards the \( \text{CO}_2 \) oxygen or carbon atom. In the first alternative, the reaction proceeds through a hydrocarboxylic intermediate (COOH) while in the second case it is via a formate (HCOO) intermediate. We have investigated the hydrocarboxylic pathway of the RWGS reaction by identifying the structures and calculating the energies of the intermediate state and two transition states (Figure 6-9).

**Figure 6-9** shows the first step of the RWGS reaction pathway where a hydrogen migrates towards its nearest \( \text{CO}_2 \) oxygen to form the hydrocarboxylic intermediate (COOH). The energy difference between the first transition state and the initial state (\((\text{CO}_2+\text{H}_2)-\text{Ni}_3/\text{YSZ}(111)\)), i.e. the activation energy, is equal to 0.85 eV. The final step involves the protonation of the hydrogenated \( \text{CO}_2 \) oxygen allowing the formation of \( \text{H}_2\text{O} \) (adsorbed on the surface) and the CO molecule (adsorbed on the Ni cluster). This step goes through a transition state with an activation energy of 1.51 eV which is higher than the first barrier (0.85 eV) meaning that the last step is the rate limiting step of the overall pathway. This large activation energy (1.51 eV) justifies the high temperature needed (above 810°C) to achieve the RWGS reaction as we stated in the introduction of this thesis.
Figure 6-9. Energy profile showing reactants, intermediates, transition states, and final products for the RWGS reaction on the Ni/YSZ(111) interface. $E_{act}$ corresponds to the activation energy between the initial and final states and the intermediate state. The energy of the reactants is set to zero. Colour key: O, Zr, Y, Ni, C, and H are respectively represented by red, grey, cyan, blue, black, and white spheres. The yellow sphere corresponds to the oxygen vacancy.

### 6.4 Chapter conclusions

We have investigated the interaction of CO$_2$ with the clean YSZ(111) surface and with the interface of supported Ni$_n$ particles ($n = 1, 4-7, 10, 20$). The molecule adsorbs weakly on the clean YSZ(111) surface and a single supported Ni atom. However, it becomes bent and activated at the interface between the Ni particle and the YSZ surface of Ni$_n$/YSZ(111) ($n = 4-7, 10, 20$) systems. The vibrational stretching and bending modes confirm the activation of the molecule along the bending mode and a shift of the asymmetrical stretching mode. The Bader charge analysis demonstrates
the charge transfer from the Ni<sub>n</sub> cluster to the molecule, with the electron density difference plot indicating a charge accumulation between the Ni atoms and the CO<sub>2</sub> molecule. In agreement with the binding energies, this electronic rearrangement is related to the strong CO<sub>2</sub> adsorption, also shown by the mixing of the metal d orbitals with the CO<sub>2</sub> molecule as described in the DOS analysis.

These observations lead us to conclude that the CO<sub>2</sub> interaction with Ni<sub>n</sub>/YSZ(111) (n = 4-7, 10, 20) interfaces are similar and independent of the Ni particle size. Therefore, because the adsorption occurs at the particle-support interface there is no need to consider clusters larger than 10 Ni atoms on the YSZ(111) surface to study their interaction with small molecules such as CO<sub>2</sub>.

Finally, we have studied the RWGS reaction where we have determined two transition states and one intermediate state (COOH) and showed that the second transition state is the rate limiting step of the overall reaction with a barrier energy of 1.51 eV.
Chapter 7

Conclusion and future works

7.1 Summary and conclusions

In this thesis we had two main goals. First, understanding, at the atomic scale, the Ni/YSZ interaction. Secondly, studying the interaction between this interface and the molecules present in the gas phase of the SOFC.

To provide insight into those two aspects, we have used first principal methods based on the density functional theory to understand the geometric and electronic structures of Ni/YSZ interface and its interaction with the gas phase molecules. We first, in chapter 3, built the most stable zirconia surface, i.e. (111), and doped it with Y atoms in order to model the YSZ(111) material. We next deposited one Ni atom on the ZrO$_2$(111) surface and on the ZrO$_2$(111) with two Y dopant concentrations, under both oxidising and neutral conditions. We observed that Ni atom prefers to adsorb on the YSZ(111) surface rather than on the ZrO$_2$(111) surface and its interaction is even stronger with the YSZ under oxidising conditions because of the electronic affinity of the system. By analysing the density of states, the charge and the electron density difference we showed that the Ni atom transfers charge to the surface atom and adsorbs away from the Y atoms when the surface is doped. On the stoichiometric YSZ(111) surface, Ni sits preferentially on the oxygen vacancy.
The conclusions above provided us insight into the Ni-oxide interaction and allowed us to build Ni clusters on both ZrO$_2$(111) and YSZ(111) surfaces. Indeed, in chapter 4 we have adsorbed Ni$_n$ (n=2-10) clusters on the later surfaces and positioned the clusters away from the Y atoms when the surface is doped. We have showed that the uppermost oxygen surface atoms stabilises the Ni cluster and these atoms are shifted from their initial position. On both ZrO$_2$(111) and YSZ(111) surfaces we have tried a flat and pyramid Ni cluster shape and from geometry optimisation results we showed that the metal clusters prefer to adopt the pyramid shape. On the YSZ(111) surface, the uppermost oxygen surface atoms are pushed towards neighbouring vacancies which could be a drawback in, for instance, SOFC since the role of theses vacancies is to transport oxygen. From charge analysis, we have also shown that upon Ni pyramid cluster adsorption, on both ZrO$_2$(111) and YSZ(111), there is a charge transfer from the Ni atoms bonded to the surface to the surface atoms. We also observed a charge transfer from the Ni atoms at the bottom of the pyramid towards the top pyramid atoms. This charge rearrangement within the metal cluster could play a role in the adsorption of the molecules at the triple phase boundary of the Ni/YSZ cermet: for example, an electrophile molecule would adsorb on top of the pyramid rather than on the meeting point between the metal cluster and the oxide surface. We have also analysed single Ni atom diffusion on both ZrO$_2$(111) and YSZ(111) surfaces thanks to the analysis of clustering and cohesive energies, and hoping rates. From this analysis, we showed, at the atomic scale, that the nucleation of Ni atoms can take place on both ZrO$_2$(111) and YSZ(111) surfaces under the SOFC experimental conditions.
After determining the nature of the Ni-oxide surfaces interaction we started adding molecules to our system in order to investigate the interactions between the SOFC gas phase molecules and the Ni/YSZ interface. In chapter 5 we considered both naked ZrO₂(111) and YSZ(111) surfaces and the surfaces with one Ni atom adsorbed on top. We described the interaction of these four systems (ZrO₂(111), YSZ(111), Ni₁/ZrO₂(111), and Ni₁/YSZ(111)) with three molecules present in the SOFC reactions, i.e. H₂O, CO₂ and CO. We have noted that H₂O adsorbs dissociatively on ZrO₂(111) but on Ni₁/ZrO₂(111) both dissociated and molecular H₂O can coexist. On YSZ(111) and Ni₁/YSZ(111) molecular H₂O is adsorbed. CO₂ shows a weak adsorption on all the surfaces except on Ni₁/ZrO₂(111) where we observed an activation of the molecule. For CO molecule, the adsorption is influenced by the presence of the Ni atom as the interaction is much stronger for Ni₁/ZrO₂(111) and Ni₁/YSZ(111) than ZrO₂(111) and YSZ(111). These molecules-surface interaction is an approximate model as we considered only one Ni atom. We therefore, in the last part of the investigation, considered large Ni clusters on the oxide surfaces and their interaction with CO₂ molecule.

In chapter 6, we have adsorbed CO₂ on Niₙ/YSZ(111) (n=1, 4-7, 10, 20) interfaces and by analysing the geometry, the electronic structure, and the vibrational modes we confirmed that the molecule is activated. Indeed, a charge transfer was observed from the cluster to the molecule and a mixing of the metal d orbitals with the CO₂ molecule was described. This CO₂ activation is observed only on Niₙ/YSZ(111) (n= 4-7, 10, 20) as on the clean YSZ(111) and the Ni₁/YSZ(111) the adsorption is weak. The geometry
and electronic structure in the CO$_2$-Ni$_n$/YSZ(111) ($n=4$-$7$, 10, 20) are similar: CO$_2$ molecule adsorbs on the edge of the metal cluster with a slight interaction with the surface atoms. This interaction is due to the mixing of the Ni d orbitals with the CO$_2$ molecule. As the interaction is independent of the cluster size we reached the conclusion that modelling the interaction of Ni/YSZ with small molecules such as CO$_2$, using density functional theory techniques, does not require to consider clusters larger than 10 Ni atoms on the YSZ(111) surface. We have therefore added H$_2$ molecule to the system and studied the reverse water gas shift reaction on Ni$_5$/YSZ(111). We have considered a reaction pathway where a hydrocarboxylic intermediate and two transition states were determined. The second transition state was the rate limiting step of the overall reaction.

### 7.2 Future works

Concerning the first aim of this thesis, i.e. analysing the Ni/YSZ interface, we have observed Ni clustering and a potential solution to this aggregation is to introduce a dopant in the oxide surface in order to trap the metal cluster. We could also reconstruct the oxide surface and consider, for instance, a step surface where the Ni adsorption would be more stable. The diffusion of larger clusters, on top of the surface, can also be considered by using molecular dynamics techniques. Molecular dynamics will allow us to take into account the effect of the temperature on the clustering of the Ni particles. Indeed, by using molecular dynamics simulations, we could describe the sintering process at the working temperature of the SOFC, i.e. approximately 700°C.
Regarding the second objective of this work, i.e. analysing the interaction of Ni/YSZ with the gas phase molecules, we would like to extend the investigation of the reverse water gas shift reaction by determining another pathway: we could consider a formate intermediate pathway in addition to the hydrocarboxylic intermediate pathway. We will determine which one is the more favourable by comparing the energy profile and the transition states of both pathways. This can also be compared with experimental data: determining the infra-red spectra of the intermediate states of both pathways and comparing them with experimental values will help to describe the geometry of the actual adsorbed intermediates at the Ni/YSZ interface and therefore define which is the most favourable pathway.

We could also study the reverse water gas shift reaction for different cluster sizes to investigate if the size of the Ni clusters affects the energy profile of the reaction pathways. The reverse water gas shift reaction can be modelled considering a cluster different from Ni to understand the role of the metal cluster in the reactions occurring at the triple phase boundary.

The activation energies determined by DFT calculations can also be used in microkinetic models. Indeed, by determining the transition states of the different elementary reactions we can evaluate the activation energies and therefore the reaction rates. It is thus possible to calculate the concentration of the different species in the system. Mikrokinetics also allow the evaluation of the reaction rates for different temperatures, which will provide a better description of the concentration of the different species at the working temperature of the SOFC.
Another challenge that can be overcome is the calculation of the Raman spectra of the different molecules involved in the reactions in the SOFC. They can be calculated and compared with experimental spectra during the operation of the SOFC. Thus, by comparing theoretical with experimental spectra, we could describe the different reactants, products, and intermediates that are present in the SOFC during the cell operation.

Furthermore, in order to understand the oxygen diffusion in the YSZ material and its role in the reactions occurring at the TPB, we could use either molecular dynamics or microkinetics simulations to study the oxygen diffusion and describe its interaction with the molecules adsorbed at the TPB. This oxygen diffusion takes place within the anode material but also within the electrolyte and the cathode. It is therefore important to describe the interface between the different components of the SOFC, which will facilitate the analysis of oxygen diffusion at these interfaces.
Chapter 8

Appendix

8.1 Figures and tables related to chapter 3

This section contains the relative energies of the 10 configurations of vac-Zr$_{10}$Y$_2$O$_{23}$(111) (Figure 8-1 and Table 8-1) and the binding energies at the non-equivalent initial adsorption sites for Ni atom on Zr$_{11}$Y$_{top}$O$_{24}$(111) (Figure 8-2 and Table 8-2), Zr$_{11}$Y$_{sub}$O$_{24}$(111) (Figure 8-3 and Table 8-3), Zr$_{10}$Y$_2$O$_{24}$(111) (Figure 8-4 and Table 8-4) and vac-Zr$_{10}$Y$_2$O$_{23}$(111) (Figure 8-5 and Table 8-5)
Figure 8-1. 10 possible configurations of vac-$\text{Zr}_{10}\text{Y}_2\text{O}_{23}(111)$, considering the O vacancy either at the Nearest Neighbour (NN) or the Next Nearest Neighbour (NNN) sites of the 2 Y atoms. Colour key: red, grey and cyan spheres correspond to oxygen, Zr, and Y atoms, respectively. The oxygen vacancy is represented by an orange sphere.
Table 8-1. Relative energies and average distances of the 9 configurations shown in Figure 8-1.

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<th>Configuration</th>
<th>Relative energy (eV)</th>
<th>Average Distances (Å)</th>
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</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
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Figure 8-2. 19 non-equivalent initial adsorption sites for Ni atom on Zr$_{11}$Y$_{29}$O$_{24}$(111) (top view).

Colour key: red, grey and cyan spheres correspond to oxygen, Zr, and Y atoms, respectively.
Table 8-2. Binding energy of the 19 non-equivalent initial adsorption sites for Ni atom on Zr$_{11}$Y$_{24}$O$_{24}$(111).

<table>
<thead>
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<tr>
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<tr>
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Figure 8-3. 20 non-equivalent initial adsorption sites for Ni atom on Zr$_{11}$Y$_{24}$O$_{24}$(111) (top view). Colour key: red, grey and cyan spheres correspond to oxygen, Zr, and Y atoms, respectively.
Table 8-3. Binding energy of the 20 non-equivalent initial adsorption sites for Ni atom on Zr$_{11}$Y$_{11}$O$_{24}$(111).

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<th>Initial Adsorption site</th>
<th>Binding energy (eV)</th>
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Figure 8-4. 52 non-equivalent initial adsorption sites for Ni atom on Zr$_{10}$Y$_2$O$_{24}$(111) (top view).

Colour key: red, grey and cyan spheres correspond to oxygen, Zr, and Y atoms, respectively.
Table 8-4. Binding energy of the 52 non-equivalent initial adsorption sites for Ni atom on Zr$_{10}$Y$_2$O$_{24}$(111).

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Figure 8.5. 38 non-equivalent initial adsorption sites for Ni atom on $\text{VAC} \cdot \text{Zr}_{10} \text{Y}_{2} \text{O}_{23}(111)$ (top view).

Colour key: red, grey and cyan spheres correspond to oxygen, Zr, and Y atoms, respectively. The oxygen vacancy is represented by an orange sphere.
Table 8-5. Binding energy of the 38 non-equivalent initial adsorption sites for Ni atom on VAC-Zr$_{10}$Y$_2$O$_{23}$(111) (top view).

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<th>Binding energy (eV)</th>
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8.2 Figures related to chapter 4

This section contains the less stable configurations and their respective binding energies of Ni clusters on ZrO$_2$(111) (Figure 8-6 to Figure 8-10) and YSZ(111) (Figure 8-11 to Figure 8-26) surfaces.
Chapter 8: Appendix

Figure 8-6. Top views (with side views as inset) of the less stable configurations of the Ni$_6$/ZrO$_2$(111) system. The binding energies are in parenthesis. Colour key: red, grey, and blue spheres correspond to oxygen, Zr and Ni atoms, respectively.
Figure 8-7. Top views (with side views as inset) of the less stable configurations of the Ni$_7$/ZrO$_2$(111) system. The binding energies are in parentheses. Colour key: red, grey, and blue spheres correspond to oxygen, Zr and Ni atoms, respectively.
Figure 8-8. Top views (with side views as inset) of the less stable configurations of the Ni$_8$/ZrO$_2$(111) system. The binding energies are in parenthesis. Colour key: red, grey, and blue spheres correspond to oxygen, Zr and Ni atoms, respectively.
Figure 8-9. Top views (with side views as inset) of the less stable configurations of the Ni$_9$/ZrO$_2$(111) system. The binding energies are in parenthesis. Colour key: red, grey, and blue spheres correspond to oxygen, Zr and Ni atoms, respectively.
Figure 8-10. Top views (with side views as inset) of the less stable configurations of the Ni$_{10}$/ZrO$_2$(111) system. The binding energies are in parenthesis. Colour key: red, grey, and blue spheres correspond to oxygen, Zr and Ni atoms, respectively.
Figure 8-11. Top views (with side views as inset) of the less stable configurations of Ni\textsubscript{2}/YSZ(111) systems. The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-12. Top views (with side views as inset) of the less stable configurations of Ni/YSZ(111) systems. The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8.13. Top views (with side views as inset) of the less stable configurations of Ni/YSZ(111) systems (flat configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-14. Top views (with side views as inset) of the less stable configurations of Ni/YSZ(111) systems (pyramid configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-15. Top views (with side views as inset) of the less stable configurations of Ni$_5$/YSZ(111) systems (flat configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-16. Top views (with side views as inset) of the non stable configurations of Ni$_5$/YSZ(111) systems (pyramid configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-17. Top views (with side views as inset) of the less stable configurations of Ni$_6$/YSZ(111) systems (flat configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-18. Top views (with side views as inset) of the less stable configurations of NiO/YSZ(111) systems (pyramid configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-19. Top views (with side views as inset) of the less stable configurations of Ni$_7$/YSZ(111) systems (flat configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-20. Top views (with side views as inset) of the less stable configuration of Ni\textsubscript{y}/YSZ(111) system (pyramid configuration). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-21. Top views (with side views as inset) of the less stable configurations of Ni$_8$/YSZ(111) systems (flat configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-22. Top views (with side views as inset) of the less stable configurations of Ni₈/YSZ(111) systems (pyramid configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8.23. Top views (with side views as inset) of the less stable configurations of Ni$_9$/YSZ(111) systems (flat configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-24. Top views (with side views as inset) of the less stable configurations of Ni$_8$/YSZ(111) systems (flat configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.

Figure 8-25. Top views (with side views as inset) of the less stable configuration of Ni$_{10}$/YSZ(111) system (flat configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.
Figure 8-26. Top views (with side views as inset) of the less stable configuration of Ni$_{10}$/YSZ(111) system (pyramid configurations). The binding energies are in parenthesis. Colour key: red, grey, blue and cyan spheres correspond to oxygen, Zr, Ni and Y atoms, respectively. The oxygen vacancy is represented by a yellow sphere.

8.3 Figures and tables related to chapter 5

This document contains the binding energies at the non-equivalent adsorption sites for H$_2$O, CO$_2$ and CO molecules on ZrO$_2$(111) (Figure 8-27 and Table 8-6), Ni/ZrO$_2$(111) (Figure 8-28 and Table 8-7), YSZ(111) (Figure 8-29 and Table 8-8) and Ni/YSZ(111) (Figure 8-30 and Table 8-9). We have not reported here the zero point energy. This document also contains the Zr$_x$O$_y$H$_z$ clusters studied in Ref. (Hornebecq et al. 2011) and discussed in our manuscript (Figure 8-31).
Figure 8-27. 4 non-equivalent initial adsorption sites for H$_2$O, CO$_2$ and CO molecules on ZrO$_2$ (111) (top view). Colour key: red and grey spheres correspond to oxygen and Zr, respectively.

Table 8-6. Binding energies (in eV) of the 4 non-equivalent initial adsorption sites for H$_2$O, CO$_2$ and CO molecules on ZrO$_2$ (111).

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Figure 8-28. 2 non-equivalent initial adsorption sites for H$_2$O, CO$_2$ and CO molecules on Ni/ZrO$_2$ (111) (top view): at the triple phase boundary (TPB) and on top of the Zr (T1) which is the most favourable adsorption sites for the three molecules on the clean ZrO$_2$(111) surface. Colour key: red, grey and blue spheres correspond to oxygen, Zr and Ni respectively.

Table 8-7. Binding energies (in eV) of the 2 non-equivalent initial adsorption sites for H$_2$O, CO$_2$ and CO molecules on Ni/ZrO$_2$ (111).

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Figure 8-29. 5 non-equivalent initial adsorption sites for H$_2$O, CO$_2$ and CO molecules on YSZ (111) (top view). Colour key: red, grey and cyan spheres correspond to oxygen, Zr, and Y respectively. The oxygen vacancy is represented by the yellow sphere.

Table 8-8. Binding energies (in eV) of the 5 non-equivalent initial adsorption sites for H$_2$O, CO$_2$ and CO molecules on YSZ (111).

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Figure 8-30. 2 non-equivalent initial adsorption sites for H₂O, CO₂ and CO molecules on Ni/YSZ (111) (top view): at the triple phase boundary (TPB) and on top of the Zr (T₁) and oxygen (T₂) which are the most favourable adsorption sites for H₂O and CO₂, and CO molecules on the clean YSZ (111) surface, respectively. Colour key: red, grey, cyan and blue spheres correspond to oxygen, Zr, Y and Ni respectively. The oxygen vacancy is represented by the yellow sphere.

Table 8-9. Binding energies (in eV) of the 2 non-equivalent initial adsorption sites for H₂O, CO₂ and CO molecules on Ni/YSZ (111).

<table>
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<th>Molecules</th>
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<td>T₂</td>
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</table>
Figure 8-31. Representation of the Zr\textsubscript{x}O\textsubscript{y}Hz clusters studied in Hornebecq et al. (Hornebecq et al. 2011) and discussed in chapter 5. Adapted with permission from V. Hornebecq, C. Kn, P. Boulet, B. Kuchta, P.L. Llewellyn, Adsorption of Carbon Dioxide on Mesoporous Zirconia: Microcalorimetric Measurements, Adsorption Isotherm Modeling, and Density Functional Theory Calculations, J. Phys. Chem. C. 115 (2011) 10097–10103. Copyright (2011) American Chemical Society.
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