Using Ferroelectrics to Tackle Fundamental Challenges in Catalysis

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Chapter 1

Introduction

Since the 1920's the emergence and development of the quantum theory of matter helped build a self-consistent and predictive mathematical framework that made it possible to understand the behavior of matter on atomic scales. Since then, quantum mechanics has helped unveil new phenomena and aspects of nature, and it has revolutionized every aspect of our way of life. Electronic devices, nuclear energy, nanotechnology, superconductivity, lasers, photonics, solar cells and MRI imaging are only few examples of important technological applications of the quantum theory of matter.

Quantum mechanics has helped us develop and understand very useful concepts including the nature of chemical bonds, thermal, electric, magnetic and optical properties of matter, and it has helped us interpret experimental results and understand them based on more fundamental physics, e.g., the electronic band structure of matter and quantum statistics. Nevertheless, the direct and accurate application of quantum mechanics to many-body systems has been an extremely challenging task for physicists and chemists. Despite having a straightforward mathematical framework based on simple interactions and laws, quantum mechanical equations become extremely difficult to solve exactly for bulk matter, surfaces or interfaces. It is only in the last few decades that with the help of a) improved computational facilities and methods, and b) development of new theories (such as density functional theory, which captures the important quantum mechanical effects yet is simple enough to be numerically solvable) that a bottom-up application of quantum mechanics to material physics and chemistry is gradually turning into a daily reality. Such a bottom-up approach allows for first principles material design: beginning from the fundamental interactions among electrons and nuclei constituting matter, one uses no adjustable parameters or fittings and quantitatively predicts the properties of a many body system. A first principles material design process allows a theorist to search a large set of possible materials or processes and select ones which show the optimum behavior for the specific application in mind. During this optimization process, the theorist learns more about how fundamental electronic, structural or chemical properties of a material affect the favorable properties being searched for: this can turn the optimization into an intelligent and controlled design process rather than brute force trial-and-error.

A brilliant example of such a bottom-up first principles materials design process is the descriptive theory of heterogeneous catalysis on transition metals [1]. In addition to deepening our knowledge about microscopic processes and mechanism involved in heterogeneous catalysis, it has helped design and modify catalysts for important technological processes including ammonia synthesis, steam reforming and CO hydrogenation [2]. The descriptive theory of heterogeneous catalysis on transition metals has also helped us identify fundamental limitations on catalytic efficiency of current catalytic materials and processes. The need for a new class of materials or processes that can go beyond these limitations is deemed necessary [1, 3].

In this work, using density functional theory (DFT) and a first principles material design, we first discuss the fundamental limitations on catalytic activity of current methods and materials and what has been discovered as the main roots of these limi-

tations. Then we discuss how one might be able to tackle some of these challenges by employing specific electronic properties of ferroelectric materials. Ferroelectricity was discovered in 1920 by Valasek in Rochelle salt (NaKC₄H₄O₆·4H₂O), which was known at the time for its piezoelectric and pyroelectric properties [4, 5]. Ferroelectricity in oxides was first discovered in BaTiO₃ in 1945 by Wul and Goldman in the Soviet Union and von Hippel in the United States [6]. Ferroelectricity can be thought of as the electric counterpart of ferromagnetism: i.e., the material possesses a bulk order parameter, called electric polarization, which is a non-zero average dipole moment per unit cell, that is switchable and adjustable using external fields, including electric field and temperature. Novel technological applications of ferroelectrics range from ferroelectric RAMs (FRAMs) [7] and ferroelectric tunnel junctions [8] to electro-optic devices [9]. Since the 1960's, the chemical and catalytic properties of ferroelectric also have been the subject of many works in the literature.

Here, we also focus on switchable catalytic and chemical surface properties of ferroelectrics. After a brief review of the theoretical methods (Chapter 2) used in this work, we outline the current fundamental challenges in catalysis (Chapter 3), discuss specific examples of efficiently catalyzing some of the most challenging industrially important chemical reactions, including water splitting (Chapter 4) and NO_x direct decomposition (Chapter 5 and 6), using ferroelectric materials in a dynamic fashion (under periodic perturbations by external fields). We end this work by laying out our plans for future research in this field (Chapter 7), including a search for an efficient catalyst for direct partial oxidation of methane.

Chapter 2

Methods

2.1 Density Functional Theory (DFT)

An attempt to directly tackle the problem of N interacting electrons in a lattice is computationally doomed to fail. To illustrate the issue, we can consider the Hamiltonian of N electrons in the Born-Oppenheimer approximation (which states that the motion of atomic nuclei and electrons in a lattice can be separated due to their large difference in mass): the electronic Hamiltonian in atomic units is

$$H = T + V_{ee} + V_{ei} (2.1.1)$$

$$T = -\frac{1}{2} \sum_{j=1}^{N} \nabla_{j}^{2}, \ V_{ee} = \frac{1}{2} \sum_{j \neq k}^{N} \frac{1}{|r_{j} - r_{k}|}, \ V = \sum_{j=1}^{N} v(r_{j})$$
(2.1.2)

$$v(r) = -\sum_{J} \frac{Z_{J}}{|r - R_{J}|}$$
(2.1.3)

In equations above, the potential v(r) is created by the fixed ions and T is the kinetic energy operator. The ions have charges $Z_I e$ and are at positions R_I . One should also note that the kinetic energy operator (T) and electron-electron interaction

operator (V_{ee}) are material independent, and the only part of the Hamiltonian that depends on specifics of a material is v(r).

If we try to find the ground state wave function Ψ_0 of this Hamiltonian,

$$H\Psi_0 = E_0\Psi_0,$$

then such a direct approach requires us to tabulate the values of Ψ_0 for each configuration of electrons over a discrete set of states, e.g., a discrete grid of electron coordinates $\{r_j\}$. If each r_j takes values on a grid of size g, then just to store Ψ_0 we will need to tabulate $\sim g^N$ values: this is an exponential function of the number of electrons! There is no hope of tackling problems with more than just a few electrons using this method.

Now the question is do we really want all the information in Ψ_0 , which includes the detailed motion and correlations of all electrons simultaneously? The answer is no: what we physically care about are usually just a few numbers:

- The ground state energy E_0 (a number)
- The band energies and gaps (a few numbers)
- The electron density n(r) (a function of 3 variables)

• Perhaps the pair probability functions P(r, r'): the probability to find one electron at coordinate r and the other one at r' (two variable function).

Density functional theory (DFT), which is based on 3 main theorems, offers a way to calculate the information we want about the electronic ground state and avoids calculating extra information in each step of the calculation. Thus, DFT offers a computationally approachable problem to solve with greatly reduced dimensionality. DFT deals directly with the ground state problem by reducing the problem of Ninteracting electrons in the lattice to a single electron problem in which each electron can be treated independently. A fundamentally important quantity in this theory is the 3-dimensional electron density n(r) which, as the theory proves, is an object that once found uniquely determines other information about the ground state. This quantity is defined as follows:

$$n(r) = N \int dr_2 \dots \int dr_N |\Psi_0(r, r_2, \dots, r_N)|^2$$
(2.1.4)

DFT is founded on three main theorems: a) The first Hohenberg-Kohn (HK) theorem, b) The second HK theorem, and c) Kohn-Sham equations. Below we discuss each briefly.

2.1.1 The first Hohenberg-Kohn (HK) theorem

The first Hohenberg-Kohn theorem (1964) states that the ground state electron density (eq. 2.1.4) uniquely determines all properties of the system, including the energy and wave function of the ground state [10]. This means that the mapping from ionic potential v(r) to the ground-state density n(r) is invertible in principle:

$$v(r) \leftrightarrow H \leftrightarrow E_0, \Psi_0 \leftrightarrow n(r)$$
 (2.1.5)

This is an important result as it means there is a good 3-dimensional variable n(r)that we can work with to find ground state properties of the material rather than the 3N dimensional wave functions. This theorem also states that the ground state energy can be written as a functional of n(r):

$$E_0[n] = \langle \Psi_0[n] | T + V_{ee} | \Psi_0[n] \rangle + \int dr \, n(r) v(r) = F[n] + \int dr \, n(r) v(r) \qquad (2.1.6)$$

Here $F[n] \equiv \langle \Psi_0[n] | T + V_{ee} | \Psi_0[n] \rangle$ is a universal function that is the same for all electronic systems and only depends on the electron density. Although this theorem rigorously guarantees that such a functional of electron density exists, it does not tell us what the functional actually is, nor does it tell us how to find the ground-state density.

2.1.2 The second Hohenberg-Kohn (HK) theorem

Let us suppose that $\tilde{n}(r)$ is a trial density: define the variational energy functional

$$\varepsilon_{v}[\tilde{n}] \equiv \int dr \,\tilde{n}(r)v(r) + F[\tilde{n}]$$
(2.1.7)

This second HK theorem [10] states that this functional takes its minimum value at the ground-state electron density n(r) associated with v(r), and its value is the ground-state energy $E_0[n]$. According to the first theorem, the density $\tilde{n}(r)$ corresponds to some $\tilde{v}(r)$ and therefore some $\Psi_0[\tilde{n}]$; then according to the variational principle:

$$\varepsilon_v[n] = E_0[n] = \langle \Psi_0[n] | H | \Psi_0[n] \rangle \le \langle \Psi_0[\tilde{n}] | H | \Psi_0[\tilde{n}] \rangle = \varepsilon_v[\tilde{n}]$$
(2.1.8)

and obviously the minimum is achieved for $\tilde{n} = n$.

We can rewrite $F[\tilde{n}]$ in eq. 2.1.7 in the following manner:

$$F[n] = \langle \Psi_0[n] | T + V_{ee} | \Psi_0[n] \rangle$$

= $T_s[n] + E_H[n] + E_{xc}[n]$
= $T_s[n] + \frac{1}{2} \int dr \int dr' \frac{n(r)n(r')}{|r - r'|} + E_{xc}[n]$

In which T_s , E_H and E_{xc} are defined as following:

- T_s is the kinetic energy of a non-interacting electron system with density n(r)
- E_H is the classical electrostatic repulsion between electrons with density n(r). This is known as the Hartree energy.

• E_{xc} is basically what is left over i.e., the quantum mechanical effects due to the electron-electron interaction that is not captured by classical Hartree term or by the non-interacting kinetic energy.

As defined above, the T_s term is defined as the kinetic energy of non-interacting electrons. In order to rigorously define this term, we have to define a set of N single particle states $\{\psi_j(r)\}$ which satisfy the following:

- 1) they are orthonormal $\langle \psi_j | \psi_k \rangle = \delta_{jk}$
- 2) they yield the desired electron density $n(r) = \sum_j |\psi_j(r)|^2$
- 3) they minimize $T_s = \frac{1}{2} \sum_j \langle \psi_j | \nabla^2 | \psi_j \rangle$

2.1.3 Kohn-Sham equations

The above framework is in principle very useful since it makes all energy expressions a functional of the density. But there is no known analytical formula for the kinetic energy $T_s[n]$ which must be approximated: given that this is a large part of the total energy, any errors here are a serious problem in practice. This difficulty was solved by Kohn and sham in 1965 [11], who showed that the task of finding right electron density can be expressed in a way that involves solving a set of self-consistent eigenvalue equations, each of which involves a single electron. Most critically, the kinetic energy is the usual one we learn in quantum mechanics, so it can be computed exactly. Minimizing the energy functional in eq. 2.1.7 for a system with N electrons is equivalent to solving the Kohn-Sham equations, given below, self consistently and finding the N states with lowest energies:

$$\left[-\frac{\nabla^2}{2} + v_{eff}(r)\right]\psi_j(r) = \epsilon_j\psi_j(r) \qquad (2.1.9)$$

$$v_{eff} = v(r) + \int dr' \frac{n(r')}{|r-r'|} + v_{xc}(r)$$
 (2.1.10)

$$v_{xc}(r) \equiv \frac{\delta E_{xc}[n]}{\delta n(r)}$$
(2.1.11)

$$n(r) = \sum_{j=1}^{N} |\psi_j(r)|^2 \qquad (2.1.12)$$

2.1.4 Different approximations to the exchange-correlation functional

In principle, solving the above set of self-consistent equations provides full information on the ground state of the system of N electrons. The complexity arises when we realize that, although mathematically proven to exist, the exact universal functional F[n] (eq. 2.1.6) is actually unknown. This is essentially mother nature's exact exchange-correlation (XC) functional. Whoever finds this functional will have solved the general ground-state many-body electronic problem (and is guaranteed a fast track to the Nobel prize). Before this great discovery (ever) happens, we can still move forward and find approximations to this universal functional that yield reasonable answers for systems under consideration. The nature of any approximation, by definition, is that it only works under certain physical conditions. Several approximations for the exchange-correlation functional $E_{xc}[n]$ have been developed over the last few decades. Below we review two widely used approximations that are also used in this thesis.

2.1.4.1 Local density approximation (LDA)

In this approximation we divide our system into small volume elements d^3r about each point r, and we treat each of these elements as a uniform electron gas with density n(r). Thus, if we denote the exchange-correlation energy per electron in a uniform electron gas at density n by $\epsilon_{xc}(n)$, we will have the LDA approximation:

$$E_{xc}[n] \approx E_{xc}^{LDA} = \int d^3 r \, n(r) \epsilon_{xc}(n(r)) \qquad (2.1.13)$$

The good news is that $\epsilon_{xc}(n)$ is known analytically in various limits, has been numerically computed using Quantum Monte Carlo methods, and many accurate fits and tabulation of it exist. One can split $\epsilon_{xc}(n)$ into two parts and define:

$$\epsilon_{xc}(n) \equiv \epsilon_x(n) + \epsilon_c(n)$$

The exchange part ϵ_{xc} is analytically computable for the uniform electron gas:

$$\epsilon_x(n) = -\frac{3e^2}{4\pi} (3\pi^2 n)^{\frac{1}{3}}$$

It is the more difficult correlation part that needs tabulations.

A popular parametrization that works for all ranges of density is a result of the work of Perdew and Zunger [12]:

The simple approximations used in deriving the LDA approximation to the XC functional might make someone think that LDA would fail in most materials. But surprisingly LDA works quite well in many materials:

- Errors in cohesive and binding energies \sim few tenths of eV/atom.
- Errors in lattice parameters $\sim 2-3$ %.

The reason behind this unexpected success is still being investigated and the topic of ongoing research.

2.1.4.2 Generalized gradient approximation (GGA)

One can try to improve the LDA approximation by including terms (at each element of volume d^3r around point r) that are a function of both $\nabla n(r)$ and n(r). This is known as the Generalized Gradient Approximation (GGA):

$$E_{xc}^{GGA} = \int d^3r \,\epsilon_{xc}^{GGA}(n(r), |\nabla n(r)|) \tag{2.1.14}$$

There is no unique recipe for creating such a functional, and the resulting form depends on the physical constraints and limiting behavior imposed on ϵ_{xc}^{GGA} . The subject of creating better GGAs is a topic of ongoing research. Broadly speaking, GGAs improve binding energies significantly. However, no improvement over LDA is found for lattice parameters.

An early version of a GGA XC functional that is still widely in use, e.g., in this thesis, is the PW91 XC functional [13]. Here the electronic exchange energy as a functional of the density is written as $E_x[n] = A_x \int d^3r n^{\frac{4}{3}}F(s)$, where $s = \frac{|\nabla n|}{2k_F n}$, $k_F = (3\pi^2 n)^{\frac{1}{3}}$, and $F(s) = (1 + 1.296s^2 + 14s^4 + 0.2s^6)^{\frac{1}{15}}$. The basis for this approximation follows from performing a gradient expansion of the exchange hole (the reduction of same-spin electron density about a particular electron due to the Pauli principle), with real-space cutoffs chosen to guarantee that the hole is negative everywhere and represents a deficit of one electron. This functional is simple enough to be applied routinely in self-consistent calculations for atoms, molecules and solids.

In 1996, Perdew, Burke and Ernzerhof devised a new GGA functional (PBE) in a work entitled "Generalized Gradient Approximation Made Simple" [14]. In contrast to the construction of the PW91 functional, which was designed to satisfy as many exact conditions as possible, PBE satisfies only those which are energetically significant. The authors claimed that the PBE solved 6 problems of the PW91, including its long derivation, its dependence on a mass of details, and its overparametrization, while also improving the description of the linear response of the uniform electron gas and giving a correct behavior under uniform scaling. Despite these theoretical improvements (and in agreement with our own calculations), PBE does not significantly improve on binding energies relative to PW91. In 1998, Zhang and Yang wrote a very short paper as a comment to the 1996 paper of Perdew-Burke-Ernzerhof and announced that a slight revision of a single parameter in the PBE functional systematically improves atomization energies for a large database of small molecules [15]. This functional is named revPBE. In 1999, Hammer, Hansen and Norskov showed that revPBE improves the chemisorption energetics of atoms and molecules on transition-metal surfaces. They also developed their own version of PBE (RPBE) which is improved relative to revPBE in the sense that it fulfills the Lieb-Oxford criterion [16] (which provides a lower bound on the non-classical part of the Coulomb energy of a quantum mechanical system) locally [17]. In practice, RPBE provides the same accuracy for binding energies as revPBE.

2.1.5 Self-consistency

As one can notice in the Kohn-Sham equations (eq. 2.1.9 to 2.1.12), there is something circular about this equations: in order to be able to find the ψ_j and n(r), one should know what v_{eff} is, and in order to know what v_{eff} is one should find ψ_j 's and n(r). To break this circle, and find a self-consistent solution, one should treat the problem in an iterative manner. This approach is best depicted in Fig. 2.1.1.

2.1.6 Plane waves basis and pseudopotentials

A computationally convenient way to solve the Kohn-Sham equations (eq. 2.1.9 to 2.1.12), is to write the single particle Bloch wave functions in a basis of plane waves (i.e., a Fourier series):

$$\psi_{nk}(r) = e^{ikr} \sum_{G}^{|G| \le G_{cut}} c_{nk}(G) e^{iG.r} / \Omega$$
(2.1.15)

where $c_{nk}(G)$ are expansion coefficients, and Ω is the unit cell volume. The expansion has to be truncated at finite G_{cut} to keep the computational expense finite.



Figure 2.1.1: In order to solve the Kohn-Sham equations self-consistently and derive the ground state electron density and single particle wave functions, one has to solve these equations iteratively: beginning by an initial guess for n(r), calculating a new v_{eff} and solving the equations to derive new single particle wave functions and new electron charge density, and continuing this loop until one reaches a stationary solution for n(r). Figure reproduced with permission from lecture notes of Sohrab Ismail-Beigi for APHY 856a.

Physically, $\hbar^2 G_{cut}^2/2m$ corresponds to an energy convergence parameter called the "kinetic energy cutoff" for Kohn-Sham wave functions, or E_{cut} in short. Such an expansion has nice properties, including: a) it can systematically be improved by increasing E_{cut} , with convergence guaranteed at the limit of $E_{cut} \to \infty$ as the Fourier basis is complete, b) the kinetic energy assumes a very simple form in a Fourier basis, and c) it automatically and naturally delivers periodic boundary conditions for a crystal.

One challenge for such a representation is that in regions close to the nuclei,

the wave functions become rapidly oscillatory (due to the high kinetic energy of electrons zooming close to the nuclei). In order to describe such functions in a Fourier basis, one has to include very high wave numbers, which translates into a very high E_{cut} and enormous computational expenses. The solution to this problem is to use a pseudopotential. In pseudopotential calculations, the core electrons are removed from the calculation, and the atomic potential felt by the valence electrons close to the nuclei is modified to be very smooth in order to make the valence wave functions smooth as well. The modifications are done in a controlled manner so that the valence wave functions outside a cutoff radius (r_c) , the energy eigenvalues are reproduced exactly, and the wave functions and potentials are smooth inside the cutoff radius r_c .

2.1.7 Hellman-Feynman theorem to calculate forces

In most of the materials design and electronic structure studies, including surfaces, interfaces or defects, we don't have any knowledge of the optimized structure of the solid, *a priori*. What one would like to do in such situations is to permit the atoms to move about in a way that delivers the lower energy structure. Thus, one needs to "relax" an initially guessed structure in order to reach at the optimized structure while moving downhill in energy. Mathematically, one needs to know the forces acting on ions in the solid (i.e., negative of the energy gradient). These are defined as:

$$F_J \equiv -\frac{dE_0}{dR_J} - \frac{dE_{i-i}}{dR_J} \tag{2.1.16}$$

Where E_0 (the electronic ground-state energy) and E_{i-i} (the ion-ion repulsion) are given by:

$$E_{0} = -\frac{1}{2} \sum_{j=1}^{N} \langle \psi_{j} | \nabla^{2} | \psi_{j} \rangle + \int dr \, n(r) v_{ion}(r) + \frac{1}{2} \int dr \int dr' \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n]$$

$$n(r) = \sum_{j} |\psi_{j}(r)|^{2}$$

$$E_{i-i} = \frac{1}{2} \sum_{J \neq K} \frac{Z_{J} Z_{K}}{|R_{J} - R_{K}|}$$

One should note that the only part of energy functional of the electronic system that directly depends explicitly on the ionic positions R_J is the ionic potential v_{ion} ,

$$v_{ion}(r) = -\sum_{J} \frac{Z_J}{|r - R_J|} \; .$$

The derivatives defined above for the forces F_J are *total* derivatives: as the ions move, all energy terms, all wave functions, and the electron density change. This would make the computation of the force very difficult. However, one can use the Hellman-Feynman theorem to greatly simplify matters. The main observation is that solving the self-consistent electronic problem is equivalent to minimizing the energy E_0 over all the electronic degrees of freedom. Hence, even if the wave functions and density change when an ion moves, the energy is stationary versus such changes (at self-consistency). Therefore, when computing the derivative for the force, one only needs to find the *explicit* dependence on the ionic positions R_J .

Applying this theorem to eq. 2.1.16 yields:

$$F_J = -\frac{d[E_0 + E_{i-i}]}{dR_J} = -\frac{\partial[E_0 + E_{i-i}]}{\partial R_J} = -\int dr \, n(r) \frac{\partial v_{ion}(r)}{\partial R_J} - \frac{\partial E_{i-i}}{\partial R_J} \qquad (2.1.17)$$

This is a very nice equation, as it tells us that DFT gives us the ionic forces

for free, i.e., in order to calculate the ionic forces we do not have to consume any more significant computational power, as we already have the self-consistent ground state electronic density: we only have to insert this density into eq. 2.1.17 and directly compute the ionic forces. Being able to compute the ionic forces allows us to relax the guessed initial structure (high energy state) into a relaxed structure (all ionic forces are zero), which corresponds to a local minimum in energy in the multidimensional configuration space. But since a general and robust way of finding the global minimum of a function in a complex multi-dimensional configuration space has not yet been developed, one is always at risk of falling into a local minimum rather than finding the global minimum of the energy function. Thus, in order to be able to have confidence in what we reports as ground state for surface structures or binding of different adsorbates to the surfaces, we always try multiple different initial guesses, and we try to find several minima and select the real ground state among them. In the process, we use our physical insight of chemical binding among different species and other physical insight which makes us able to isolate the real ground state (global minimum of energy) rather than just a local minimum.

2.2 Projected density of states (PDOS) on atomic orbitals

The density of electronic states per unit energy (DOS) at energy E is formally defined as:

$$D(E) = \frac{1}{N_k} \sum_{n,k} \delta(E - E_{nk})$$
(2.2.1)

Here N_k is the number of k-points used in the sampling of the Brillouin zone, and E_{nk} are the eigenvalues of the Hamiltonian that correspond to band index n and index

k in the Brillouin zone. When applied to DFT, E_{nk} are the Kohn-Sham eigenvalues. In practice, the formula above is not useful since we have a finite sampling in kspace, so we end up with a sum of spikes in energy due to the delta functions and a very unsmooth DOS. The solution is to replace the delta function with a broadened function $g_{\sigma}(E)$ with unit area, which could be a Gaussian with a narrow width σ . Then we have:

$$D_{\sigma}(E) = \frac{1}{N_k} \sum_{n,k} g_{\sigma}(E - E_{nk})$$
 (2.2.2)

A plot of the DOS versus energy E is informative in that it gives us information such as the band gap, the band widths, the density of states close to the Fermi energy, and relative band alignment of different materials. In order to be able to obtain more information from the Kohn-Sham eigenvalues, we can define an atom specific or an orbital specific DOS which yields the individual contributions from different atoms and/or orbitals to the DOS. Such a projected DOS (PDOS) provides much valuable additional information:e.g., hybridization among different orbitals, relative weights of various orbitals in the various energy bands, the nature of chemical interactions in the system, and the chemical properties of surfaces and interfaces. The PDOS for atomic orbital α on atom I, which identifies a unique atomic orbital $\phi_{\alpha}^{I}(r)$, is defined as:

$$D_{\sigma}^{I,\alpha}(E) = \frac{1}{N_k} \sum_{n,k} |\langle \phi_{\alpha}^I | \psi_{nk} \rangle|^2 g_{\sigma}(E - E_{nk})$$
(2.2.3)

Examples of the use of various PDOS in analysis of electronic structure will be provided in the following chapters.

2.3 Nudged Elastic Band (NEB) method to find reaction barriers

The nudged elastic band (NEB) method [18, 19, 20, 21] is a technique to find the minimum energy path (MEP) that connects two minima in the energy landscape: a smooth and differentiable path in configuration space along which the maximum value of the energy is the smallest (among all conceivable paths between the two points). For N particles each embedded in 3-dimensional space, the configuration space is 3Ndimensional, and finding the MEP is mathematically equivalent to finding the saddle point in the separating region (transition state or TS region) between two minima regions: reactants region (its minimum is called the initial state or IS) and products region (its minimum is called the final state or FS). This (first-order) saddle point is the minimum of energy in 3N-1 dimensional TS hyperplane (perpendicular to reaction coordinate), and a maximum in 1 direction (reaction coordinate). In this picture both the IS and FS regions, which are basins of attraction, are 3N dimensional objects separated by the TS. Within the harmonic approximation to transition state theory (HTST), in which a harmonic expansion is used around IS, FS and TS, and within the limit that the vibrational frequencies are much smaller than $\frac{k_B T}{h}$, the rate constant of the reaction reduces to an Arrhenius type expression [22]:

$$k_{Arrhenus} = \nu \cdot e^{-\frac{\Delta E_a}{K_B T}} \tag{2.3.1}$$

in which $\Delta E_a = E_{TS} - E_i$. In such an approximation, ν is usually assumed to be $\sim \frac{k_B T}{h} \sim 10^{13} \text{ s}^{-1}$ which is representative of a typical molecular vibration frequency.

The NEB method takes as input an initial discretized guess to the MEP consisting of, e.g., ~ 10 "images" connecting the IS and FS: each image is a replica of the system of interest which its own set of atomic coordinates. The NEB algorithm then tries to relax these images to lie on the true MEP. The most naive form of relaxation would cause the images in the reactant region to fall into the IS and the ones on in the product regions to fall into F. In order to prevent this, the NEB method assumes that successive images are connected by fictitious springs with Hookian spring constant k: thus this string of images (a discrete representation of a trial path) can relax to its least stretched state once it is going through the MEP. A special relaxation process takes place where one defines two distinct directions in configuration space: a) the direction parallel to the path (denoted by ||), and b) the direction perpendicular to the path (denoted as \perp). The relaxation of images perpendicular to the path minimizes sum of total energies of the images, while the motion in the direction of path is relaxed according to the fictitious springs:

$$F_i = F_{i\parallel}^s + \nabla E(R_i)_\perp \tag{2.3.2}$$

$$\nabla E(R_i)_{\perp} = \nabla E(R_i) - (\nabla E(R_i) \cdot \hat{\tau}_i)\hat{\tau}_i \qquad (2.3.3)$$

$$F_{i\parallel}^{s} = k(|R_{i+1} - R_{i}| - |R_{i} - R_{i-1}|)\hat{\tau}_{i}$$
(2.3.4)

where F_i is the total force on image i, $\hat{\tau}_i$ is the local tangent to the path, $\nabla E(R_i)$ are physical forces on the image due to the true energy function, and F_i^s are the forces due to the fictitious springs connecting successive images.

There are two modifications to the general picture given above that make the NEB method more robust in finding a good approximation to the saddle point (the minimum of the TS region which is also the highest point on the MEP):

• variable spring constants: instead of a fixed spring constant k for all images, one can assume values between a lower and upper bound (which are often about an order of magnitude different). This modification can give more resolution in determining the path and the local tangent vectors $\hat{\tau}_i$ where one wants it most which is close to the saddle point (this is achieved by putting stiffer springs near the saddle point to "bunch up" the images there).

• climbing image: Here the highest energy image follows a different dynamic and is forced up to the saddle point. This image does not feel the spring forces along the band. Instead, the true force at this image along the tangent to the current path (approximate MEP) is inverted. Consequently, the image maximizes its energy along the current path and minimizes it in all other directions. When it converges to a final path, this method is guaranteed to put exactly one image on the saddle point.
Chapter 3

Fundamental challenges of catalysis

3.1 Introduction

Surface catalysis based on transition metals and their alloys has been one of the most important research fields in theoretical and experimental catalysis and chemistry [23, 24]. In addition to basic scientific discoveries, this field has had enormous impacts on daily lives, e.g., it has helped overcome the world hunger problem by introducing the Haber-Bosch process to efficiently break the strong N₂ triple bond and synthesize ammonia, which is the most important precursor for fertilizers [25, 26]. A significant breakthrough for transition metal catalysis in the last few decades has been the introduction of a predictive theory for catalysis based on a combination of the d-band model, activity maps and scaling relations [27, 28, 29, 30, 3]. Having efficient computational tools and a predictive theory has permitted computational scientists to design novel catalysts and computationally screen materials for a specific functionality, and this has been followed by attempts to experimentally fabricate the promising candidates [31, 32, 33]. Recent computational and theoretical contributions to the field (especially by Norskov and coworkers), combined with endeavors on the experimental front, have led the field of heterogeneous catalysis from a trial-and-error

approach to a highly controlled design process [1, 3, 34]. Among the many contributions of the descriptive theory of heterogeneous catalysis has been the modification of the stability of Ni catalysts for steam reforming by the addition of gold and the mixing of cobalt and molybdenum in ammonia synthesis catalysts [35, 36, 37].

Another aspect and an achievement of the predictive and descriptive theory of heterogeneous catalysis has been its ability to identify some of the fundamental limitations of current catalytic methods and materials. Consequently, the catalysis community has been able to identify some fundamental challenges facing heterogeneous catalysis that hinder the design of more efficient catalysts for important reactions including water splitting, CO_2 reduction, ammonia synthesis and selective partial oxidation of methane to methanol. A solution to these challenges might require fundamental and revolutionary changes in catalytic materials, methods and processes and new design paradigms [1]; nevertheless, the payoff can be most rewarding: more energy efficient and cheaper methods to produce necessary chemicals for agriculture and industry, more environment friendly energy harvesting methods, and possibly a better chance of survival for human kind on a fragile planet with finite resources.

3.2 The descriptive theory of heterogeneous catalysis

Since the early 20th century, the Sabatier principle has provided us with a framework to conceptualize the idea of an optimum catalyst. This principle states that the surface adsorbate interaction should be optimal: not too weak to fail to activate the reactants, yet weak enough so that the products can leave the surface so that it can continue to catalyze (i.e., no surface poisoning). The principle is best visualized with the volcano plots which are ubiquitous in the catalysis literature (see Fig. 3.2.1).

In its original conceptual and qualitative form, the Sabatier principle cannot di-



Figure 3.2.1: Schematic illustration of the Sabatier principle. According to this principle, the surface-adsorbate interaction should be optimum: too weak or too strong an interaction will hinder the catalytic activity.

rectly be used to design catalysts. Using scaling relations, the d-band model and activity maps, the descriptive theory of heterogeneous catalysis has successfully turned the Sabatier principle into a quantitative and predictive approach that can be used to understand the microscopic processes involved in catalysis and improve or even design new catalysts [3, 1]. Below we review these concepts briefly, in order to understand the general framework of the descriptive theory of catalysis. Then we use this knowledge to identify some of the fundamental challenges facing catalysis.

3.2.1 The scaling relations

Taking the ammonia synthesis reaction $(N_2+3H_2 \rightarrow 2NH_3)$ as an example, and assuming, as both theory and experiment confirm, N_2 dissociation is the rate limiting step in this reactions: the overall reaction rate turns out to be dependent on two in principle independent parameters 1) the transition-state energy (activation barrier) and 2) the adsorption energy of atomic nitrogen. Thus, the problem of optimization of reactants and intermediates (as dictated by the Sabatier principle) is a 2-dimensional problem. A scaling relation is a correlation (confirmed by both theory and experiment) between the binding energy of different adsorbates that reduces the dimension of the optimization problem and makes the catalysis search and design problem much easier to understand and tackle. For example, in the case of ammonia synthesis it has been shown that the transition state energy and adsorption energy for atomic nitrogen are strongly correlated, thus the dimension of optimization problem is reduced from 2 to 1: the nitrogen adsorption energy can be the single variable (see Fig. 3.2.2). The scaling relation between the transition and dissociated state of a simple molecule is a specific example of scaling relations known as the Bronsted-Evans-Polanyi (BEP) relations since the 1920's. The predictive theory of transition-metal heterogeneous catalysis has shown that scaling relations are more general and are correlations among surface bond energies of different adsorbates including transition states [1, 3]. The theory has also identified the underlying mechanism leading to these correlations, which will be discussed later. Scaling relations reduce the dimension of the Sabatier optimization problem to a few-dimensional (sometimes 1-dimensional) problem described by a minimal number of parameters (binding energies) known as descriptors.

The case of ammonia synthesis was the simplest example of a scaling relation. There are many examples of scaling relations for more complex reaction networks. Hydrogenation of CO to methane, methanol or ethanol, even within a very simple model, contains 52 elementary reactions and thus at least 104 independent energy



Figure 3.2.2: Scaling relations and volcano activity map for ammonia synthesis. a) Ammonia synthesis rate as a function of nitrogen adsorption energy E_N and N_2 dissociation barrier E_{N-N} with energetics for stepped transition metal sites and the corresponding scaling relation line (dashed black-white) showing that E_{N-N} is a linear function of E_N , which prevents the metal steps from entering the optimum catalyst region (red area). The alkali-promoted scaling relation is given by the magenta line. b) Calculated rate as a function of a single descriptor of E_N . Both figures are also known as volcano plots, with the tip of the volcano being the region of the phase space with maximal catalytic activity. Reprinted from: National Science Review (2015): nwv023 by A. Vojvodic and J. K. Norskov.

variables [3], leading to a 104-dimensional optimization process which will be very hard to understand and perform and does not leave much room for physical and chemical intuition. Using scaling relations, one can reduce the dimension of the problem to only 2! The only truly independent biding energies are the binding of C and O to the surface. For example OH scales with O, while CH, CH_2 and CH_3 all scale with C, due to their similar binding mechanisms to the surface. The binding of H also scales well with C.

We have investigated some of these scaling relations for the case of N, NH, O, and OH binding to simple transition metal (001) and (0001) surfaces in order to benchmark our calculations. The results are shown in Fig. 3.2.3. It is seen that NH binding scales with N binding energy, and OH binding scales very well with O binding energy, due to their similar binding mechanism to the transition metal surface. Although the correlation is not as strong as those cases, a reasonable correlation can also be seen between N and O atomic binding energies. The results are in satisfactory agreement with the literature [38] even though they have been a) generated based on a small data set (i.e., only few metals and surfaces) and b) generated using a less elaborate exchange-correlation (XC) functional (we used PBE [14], while the most trusted results in the literature use RPBE [17]). The later can be regarded as a confirmation of the recent finding by Norskov and co-workers that the scaling relations and the position of the tip of the volcano in volcano plots is quite insensitive to the errors in calculating the electronic structure of the surface, including errors rooted in XC functional [39]. This is one reason behind the success and predictivity of the theory of heterogeneous catalysis on transition metals.



Figure 3.2.3: Scaling relations for binding of NH, N, OH, and N to transition metal surfaces, calculated using a PBE-GGA exchange correlation functional. The energies are computed relative to the atom or molecule in vacuum. Bigger numbers represent stronger binding energy, since the definition I have used to calculate the binding energies is: $E_{binding} = E(adsorbate) + E(surface) - E(adsorbate/surface)$. The equation for each scaling relation is given in boxes on the top-left corner of each plot.

3.2.2 The d-band model

One of the beauties of the descriptive theory of heterogeneous catalysis on transition metals is the existence of a microscopic mechanism at the electronic structure level that leads to the scaling relations mentioned above [40, 41]. It has been shown that the trends observed on different metals and surfaces can be understood based on a simple model in which the center of the transition metal d-band hybridizes with the adsorbate. Since the bonding is between localized states on the adsorbate and a surface transition metal atom, the center of the transition metal d-band is the appropriate energy for consideration in the bonding and hybridization. The result of this hybridization is the creation of bonding and antibonding states, below and above the Fermi energy, respectively (see Fig. 3.2.4). In this d-band model, the closer the center of the d-band is to the Fermi energy (E_F) , the more antibonding states are pushed above E_F , the more depopulated they become, and this leads to a more stable surface-adsorbate bond. Consequently, in such a model the energy separation between E_F and the d-band center becomes a good descriptor of the chemical bond (see Fig. 3.2.5 [41]. Since the binding energy of chemically similar adsorbates and their transition states depend linearly on this descriptor, there is also a linear correlation between these quantities (binding energies and activation barriers) [3]. This is the microscopic basis of the observed scaling relations. For benchmarking purposes, we have also made a graph of N binding energies versus the center of the d-band, using the values we calculated using PBE-GGA XC functional, which shows a strong linear correlation in agreement with the literature (see Fig. 3.2.6).

3.2.3 Activity maps

By combining the scaling relations (which define the descriptors for a given reaction) with a kinetic model (which is often a mean field model that connects the relative coverages, concentrations of reactants and products and turnover frequencies to the



Figure 3.2.4: Hybridization between the adsorbate states (oxygen p state specifically in this figure) and transition metal surface states for Pt(111). First the sharp atomic like states are broadened and shifted down in energy as a result of interaction with the broad metal sp states. Then, hybridization with the sharper surface d-band causes creation of bonding and antibonding states and stabilization of the chemical bond between the surface and the adsorbate. From: Hammer, Bjørk, and Jens Kehlet Nørskov. "Theoretical surface science and catalysis—calculations and concepts." Advances in catalysis 45 (2000): 71-129.

reaction rates computed from first-principles and environmental variables such as pressure of reactants and products and the temperature), one can define a mapping of catalytic activity into descriptor space. This mapping is denoted as an activity map [3]. Fig. 3.2.2 was an example of such a map, in which the system was described based on a single descriptor (nitrogen adsorption energy). Fig. 3.2.7 shows activity maps for different products in CO hydrogenation process (methane, methanol and ethanol) in which the descriptor space is 2-dimensional (Carbon and oxygen binding energies). Also it can be seen in Fig. 3.2.7 how a selectivity map is constructed by combining the activity maps for different possible products. Such a map is particularly useful for reactions that can involve different pathways leading to different products: by comparing the relative production rates, each point of such a map indicates the extent to which a product is selectively produced at that point of the phase space.



Figure 3.2.5: Correlation between the center of the d-band and adsorbate (oxygen specifically in this figure) chemisorption strength. Here, unlike the convention I have used throughout this work, more negative numbers indicate stronger bonding, since chemisorption energy is defined as $E_{binding} = E(O/surface) - \frac{1}{2}E(O_2) - E(surface)$. From: Hammer, Bjørk, and Jens Kehlet Nørskov. "Theoretical surface science and catalysis—calculations and concepts." Advances in catalysis 45 (2000): 71-129.



N binding energy correlation with center of the d-band

Figure 3.2.6: Correlation between the center of the d-band and adsorbate (nitrogen specifically in this figure) chemisorption strength, calculated using PBE-GGA exchange correlation functional. Here, like the convention I have used throughout this work, more positive numbers indicate stronger bonding, since chemisorption energy is defined as $E_{binding} = E(adsorbate) + E(surface) - E(adsorbate/surface)$.



Figure 3.2.7: Activity and selectivity maps for CO hydrogenation. a) the rate of methane formation, b) the rate of methanol formation, c) the rate of ethanol formation, and d) selectivity map for three different products (white points on this map indicate binding energies that correspond to different A_3B transition metal alloys).

3.3 Fundamental challenges of current catalytic meth-

ods and processes

Scaling relations have been one of the foundations for understanding catalytic trends: these relations help by significantly reducing the number of potentially independent degrees of freedom (e.g., the full set of binding energies of the products and intermediates) in a chemical reaction to just a few descriptors [42, 43, 44, 45, 38, 46]. However, as Vojvodic and Norskov pointed out in a recent review, despite being extremely useful, scaling relations have also helped identify some of the limitations on the tunability of many catalysts [1]. Figure 3.2.2 provides an example for the case of ammonia synthesis. Clearly, a much better catalyst for ammonia synthesis could be fabricated if one could circumvent or depart from the known scaling relations for (stepped) transition metal surfaces: the scaling relation has confined these surfaces to being far from maximally efficient. Due to this restriction, namely the reduced degrees of freedom stemming from the scaling relations, there are many reactions that cannot be fully optimized and thus suffer from inefficient catalysis. There are also some important reactions that currently have no effective catalysts (e.g., the partial oxidation of methane to methanol [47, 48, 49, 50] and the direct decomposition of NO_x [51]). The need for "an extra degree of freedom" that can take us away from the constraints of the scaling relation is clear. The quest for circumventing the scaling relations is afoot, and this may revolutionize our understanding of and methods for heterogeneous catalysis. As pointed out by Norskov and Vojvodic [1], it is unclear whether one can design or find a material system that breaks scaling relations to the degree where there is no correlation among chemically similar intermediates and transition states, but it is quite clear that current materials are too constrained in this regard.

3.4 Application and promise of ferroelectrics for catalysis

A polar surface arises when the electrical dipole associated with the bulk unit cell of a polar crystalline material has a non-zero component perpendicular to the surface i.e., $\vec{P}.\hat{n} \neq 0$, where \vec{P} is the bulk polarization vector and \hat{n} the surface normal. The emergence of bulk polarization is a consequence of the offset between the centers of the positive and negative charges in each unit cell [52, 53]. If this polarization were uncompensated, a constant electric field would develop across the material with an energy cost scaling with the thickness of the material and rapidly becoming unphysically large for thick samples. The solution is to accumulate equal amounts of compensating opposite charges ($\sigma = \pm \vec{P} \cdot \hat{n}$) on the opposing polar surfaces to cancel the interior electric field so that the energy becomes independent of thickness. This can most simply be achieved through an electronic reconstruction: electrons or holes are transferred to the surfaces to compensate the polarization charge (Fig. 3.4.1) [54, 55, 56, 57, 58, 59, 60, 61]. Over timescales where atoms move and can migrate to or away from the surfaces, an additional avenue for compensation becomes possible: atomic reconstruction. Here, atoms are adsorbed or removed from the surfaces. These adsorbates or vacancies make available additional electronic states for electrons or holes that more favorably accommodate them compared to the energy bands of the stoichiometric surfaces. Such defects then accept the electrons or holes and lower the total energy of the surface, becoming ions in the process (in some cases charged species may adsorb directly). Thus, the net effect of atomic reconstruction is to add ions to the surface that balance the polarization with a surface charge density of opposite sign and cancel the electric field inside the material.



Figure 3.4.1: Schematic illustration of two scenarios for a ferroelectric surface. a) Unphysical scenario: a large depolarizing electric field exists across the entire material created by the uncompensated surface charges stemming from ionic displacements along the polarization direction. b) Electronic reconstruction by electrons or holes for positive or negative polarization \vec{P} which results in zero net electric field inside the material.

Since the mid 20^{th} century, the intriguing possibility of dynamically controlling surface chemistry and enhancing catalytic properties has turned ferroelectric and polar materials into the subject of numerous studies. Starting in 1952, Parravano observed anomalies in CO oxidation rates over ferroelectric sodium and potassium niobates near the Curie temperature of these materials (the second order transition temperature when the polarization vanishes) [62]. Next, in the 1960s, Stadler demonstrated that ferroelectric polarization can change the physical properties of supported metal films [63, 64]. The subject received renewed attention in the 1980s when Inoue et al. studied the effect of the substrate polarization on catalytic activity of supported metals and found higher CO oxidation rates for negatively poled surfaces, which they attributed to weaker CO adsorption for metal supported on the positively poled surface [65, 66]. In the same timeframe, dramatic effects of the polarization direction on adsorption on polar, but not ferroelectric, materials were demonstrated [67, 68].

The photocatalytic properties of ferroelectrics and polar materials have also attracted significant attention in the scientific community [69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88]. As far back as 1986, Inoue et al. studied photoassisted water decomposition on lead zirconate titanate (PZT) ceramics. In these experiments, 10-40 times higher H₂ production rates were observed for positive relative to negative polarization [70]. The main underlying mechanism was determined to be the polarization-dependent band bending close to the ferroelectric surface that facilitates the separation of the electron-hole pair and, depending on the polarization direction, directs either electrons or holes to the surface (see Fig. 3.4.2). Thus, in positive polarization, enhanced electron transfer to the surface promotes the hydrogen evolution reaction.

Ferroelectric and piezoelectric materials have also been exploited in the context of turning waste vibrational energy, which is abundant in our environment (e.g., vibrations made by cars, trains or engines in general) into electricity [89, 90] using piezoelectric nanogenerators [91].

We suggest that ferroelectrics may make an important contribution in solving the



Figure 3.4.2: Schematic band structure of a BiFeO₃/TiO₂/H₂O heterostructure with the ferroelectric polarization (P_s) of BiFeO₃ (a) pointing away from the BiFeO₃/TiO₂ interface, and (b) pointing towards the BiFeO₃/TiO₂ interface. The vacuum level, conduction band edge, Fermi level and valence band edge are denoted by E_{vac} , E_c , E_f , and E_v , respectively. The hydrogen, silver, and oxygen redox levels are indicated on the right. From: Y. Zhang, A. M. Schultz, P. A. Salvador, and G. S. Rohrer, Journal of Materials Chemistry, 21(12), 4168-4174.

challenge of the extra degrees of freedom mentioned above. Ferroelectric surfaces have an added degree of freedom, which is the direction of the polarization below the surface. Furthermore, the polarization couples to multiple physical degrees of freedom, which permits different pathways to modulate the polarization: some examples include use of acoustic waves (piezoelectric effect) [92], temperature (pyroelectric effect) or external electric fields. We note that some ferroelectrics are multiferroic: their magnetic properties are coupled to their electrical polarization [93, 94, 95], so that, in principle, one can also enlarge the list of external control knobs to include magnetic fields [96, 97, 98]. The overall logic is that a ferroelectric surface has added tunability because: (i) there is an order parameter (here the ferroelectric polarization) below the surface, (ii) the order parameter concerns charge degrees of freedom and thus can couple strongly to the surface chemistry, and (iii) the order parameter can be controlled by external knobs. In principle, this may permit one to shift the scaling relations in their appropriate phase space; in practice, one needs to see if the effects are large enough to be useful and how to harness them.

A second benefit of using ferroelectrics is the potential for dynamic or cyclic behavior [61]. Namely, instead of simply using the polarization to shift scaling relations, one can envisage sidestepping some of the fundamental compromises in the usual approach to catalyst optimization: the Sabatier principle. As mentioned above, the Sabatier principle enforces a compromise situation for a fixed surface: maximum activity requires an optimal adsorbate-surface interaction strength that is neither too strong nor too weak (see Fig. 3.2.1) [3]. However, if one could cycle the surface between multiple states with very different interaction strengths, some of the compromises could be overcome: adsorption and desorption do not have to be competing effects but both can be periodically enhanced or suppressed to drive the appropriate set of reactions or adsorption/desorption processes in sequences [61].

3.5 Conclusions

The theory of heterogeneous catalysis on transition metals, erected on the foundation of the scaling relations, the d-band model, the Sabatier principle and activity maps, has been a successful theory that has enriched our knowledge of catalysis at the microscopic level and it has helped transform the field of heterogeneous catalysis from a trial-and-error approach to a controlled design process. Its predictions have been confirmed by experiments, and it has helped enhance and design catalysts with important applications in wide range of reactions from ammonia synthesis to steam reforming [36, 37, 32, 41, 33]. In addition, it has helped us understand some of the most fundamental limitations on catalytic activities of current materials and processes. The quest for extra degrees of freedom that can free us from the limitations of the scaling relations is afoot. We believe ferroelectrics, due to possessing an order parameter that is coupled to the surface chemistry and external fields (including temperature, electric, magnetic and strain fields), have a great potential to serve the catalysis community. Ferroelectric-based catalysis can also help us go beyond some of the fundamental limitations imposed by the Sabatier principle on catalytic activity of materials. In the next few chapters, we describe specific examples to illustrate how ferroelectrics can help us reach these goals and catalyze reactions which are considered challenging (in some cases impossible) for more conventional catalysis.

Chapter 4

Water splitting using ferroelectrics

4.1 Introduction

The increasing demand for renewable energy sources is a prominent challenge of the 21st century [99, 100, 101, 102]. Since the industrial revolution, the main energy sources for industrial societies have been fossil fuels. The resultant carbon emission has had significant effects on the environment [103, 104, 105, 106]. Thus, departure from carbon-based to sustainable energy sources is deemed desirable. One scenario is to harvest solar, geothermal or wasted industrial energy and to store it in the chemical bonds of molecules such as H_2 for later use as fuel [100, 99, 107]. Hydrogen has a high energy density, zero carbon emission when burned, and can be used in fuel cells to produce electricity [108, 109]. These factors make hydrogen a prominent candidate for a future energy carrier [110]. Additionally, hydrogen is a critical component of important industrial and chemical processes, including ammonia and methanol synthesis [111, 112, 113, 114]. Unfortunately, an efficient and economically viable method for green production of hydrogen is still lacking [115, 116]. At present, hydrogen is produced primarily by processing fossil fuels: e.g., oil or natural gas reforming and coal gasification [117, 118, 101]. Here, we describe the possibility of exploiting the

pyroelectric properties of ferroelectrics [119] to design a catalytic cycle that enables water splitting into hydrogen and oxygen using low/intermediate grade heat. One should note that harvesting waste heat and turning it into electrical power via the pyroelectric effect in ferroelectrics and cyclic temperature modulations (the Olsen or Ericsson cycle) [120, 121, 122, 123, 124, 125, 87, 126] is an active research area. Here, for the first time, we exploit the pyroelectric effect of ferroelectric oxides to propose a catalytic cycle that harvests waste heat and stores its energy in the chemical bonds of H_2 molecules. Unlike the Olsen cycle, our cycle does not require an external electric field [127].

Although our work is computational, there is indirect experimental evidence suggesting our proposal may work in practice: a) it is possible to harness vibrational energy to split water using piezoelectric ZnO fibers and BaTiO₃ dendrites based on what has been termed the piezoelectrochemical (PZEC) effect [128]; b) pyroelectricity in ferroelectrics can produce reactive oxygen species (ROS) in water (a pyroelectrocatalytic effect) which cannot be used for energy storage (due to their extreme instability) but can be used for water disinfection [129, 130]. These experiments show that vibrational energy or heat can be transformed into chemical energy (by dissociating water molecules). Based on our first principles results below, we believe that one should be able to produce hydrogen using the pyroelectric effect.

As mentioned in the previous chapter, by employing ferroelectric polarization in a cyclic manner (i.e., switching between the two opposite out-of-plane polarization directions), one can overcome some of the fundamental limitations on catalytic efficiency imposed by the Sabatier principle [131, 1, 61] and thus catalyze reactions that are challenging for more conventional catalysts. In this scheme, one cycles the surface between multiple states with very different interaction strengths: adsorption and desorption do not have to be competing effects (as per the Sabatier principle [3, 132] for fixed surfaces) but both can be cyclically enhanced or suppressed to drive the desired set of reactions or adsorption/desorption processes in sequence [131, 61]. Here, we study the (001) surface of ferroelectric PbTiO₃ (a canonical ferroelectric oxide exemplifying this class of materials) and describe a temperature-driven catalytic cycle which uses the pyroelectric effect [133, 134, 135, 136, 137, 138] to modify the ferroelectric polarization in a cyclic manner. This creates a process that can effectively split H₂O into H₂ and O₂. In practice, the thermal energy needed to drive this cycle may be provided by geothermal [139, 140], industrial waste heat [134, 141, 142, 143, 144, 145, 146], or concentrated solar [147, 148, 149] power: the Curie temperature (T_C) [150] of common ferroelectric perovskites (e.g., PbZr_xTi_{1-x}O₃ or BaTiO₃ solid solutions) can be tuned [151, 152, 153, 154, 155, 156] in the accessible range of 100-450 °C [157, 158, 156, 151].

Our study fills a missing link in a chain of phenomena that share a fundamental underlying theme of converting some form of waste energy (heat or vibration) into a more useful form (electricity or chemical energy) using polarization modulation. These phenomena include: Olsen cycle [134, 122, 143], piezoelectrochemistry [128, 159, 160, 161], pyroelectrocatalysis [130, 129] and piezoelectric nanogenerators [91, 90, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171]. The later are piezoelectric materials that have been been exploited in the context of turning waste vibrational energy (which is abundant in our environment e.g., vibrations made by cars, trains or engines in general) into electricity. In this work, using *ab initio* DFT calculations, we connect the polarization modulation to the microscopic structure of the polarization-dependent surface phases, and identify the driving forces behind the energy conversion.

4.2 Computational methods

We perform DFT calculations [10, 11] with plane-wave basis sets using the Quantum Espresso software [172] together with ultrasoft pseudopotentials [173, 174, 175]. A slab geometry with the (001) surface normal and polarization axis is employed [54, 61]. We introduce at least 15 Å of vacuum to isolate periodic copies of the slabs. A dipole correction in the center of the vacuum is used in order to eliminate the artificial electrical field and the unphysical dipole-dipole interactions among the copies of the slab in the z direction [176]. The plane-wave energy cutoff is 30 Ry. The k-sampling density of the Brillouin zone is 8×8 for a 1×1 primitive surface unit cell. We start all the relaxation calculations by breaking symmetries in both spatial and magnetic degrees of freedom. For each system, we consider several (sometimes up to 14) initial structures, to make it highly likely what we find is the global minimum in energy and not just a local energy minimum.

The Kohn-Sham states' occupations are smeared using the cold smearing method of Marzari and Vanderbilt with a smearing width of 5 mRy/k_B [177]. The convergence criterion on forces is that all components of all forces must be smaller than 1×10^{-3} (a.u.). The convergence threshold on pressure for variable cell calculations is p < 0.5 KBar. In each ionic relaxation step, the energy convergence threshold for selfconsistency is 1×10^{-6} Ry (in the final steps, close to the energy minimum, this value is automatically reduced by a factor of 100). These convergence parameters yield binding energies to better than 0.1 eV precision. We use a standard method whereby a few layers of Pt are placed on the bottom PbTiO₃ surface to create an electrode with a large density of states at the Fermi level, which simulates an electron reservoir that exists in realistic systems of thick ferroelectric films [54, 178, 179, 61, 180]. The energies reported here are obtained using the GGA-PW91 exchange-correlation (XC) functional [13, 14]. However, the main findings are checked to be independent of the specific choice of XC functional, as shown later in this chapter.

A sample $c(2 \times 2)$ supercell is shown in Fig. 4.2.1. The $c(2 \times 2)$ structures have in-plane periodicity in the xy plane with a square unit cell with lattice constant 5.459 Å, to model epitaxial growth on a SrTiO₃ substrate. This value for 2×2 structures is 7.72 Å. We fix the structure of the second, third and fourth atomic layers of PTO on top of the Pt electrode to their bulk values in order to simulate the mechanical boundary conditions appropriate to a thick PTO film: this leads to reasonable computational expenses and sizes of the simulation cells [54, 61]. By "bulk values" we mean the appropriate bulk atomic configuration corresponding to the desired out-ofplane polarized state. Later, for the fixed polarization calculations that are meant to compare results of different exchange-correlation (XC) functionals for a fixed substrate polarization, we fix more layers, as shown in Fig. 4.2.1 to ensure that we isolate the effect of polarization from the "pure" effect of the exchange-correlation (XC) functional on the binding energies and our phase diagrams. The reason is that the LDA XC functional predicts polarization of about 60 $\frac{\mu C}{cm^2}$ (less than 90 $\frac{\mu C}{cm^2}$ which is the experimentally measured value [181, 182]) for bulk PTO, and if only 3 atomic layers are fixed the polarization tends to decrease as we move from the bulk toward the surface (i.e., a polarization gradient appears inside the film). Thus, in order to make sure we isolate the effect of polarization from the effect of the XC functional for these calculations, we fix more PTO atomic layers (to a structure with fixed 90 $\frac{\mu C}{cm^2}$ polarization) up to the top layer (see Fig. 4.2.1).

As can be seen in Table 4.1 although the bulk structure of PTO is very well converged using a k-space sampling of $8 \times 8 \times 8$ for a five atom primitive PbTiO₃ cell but it strongly depends on the E_{cut} , and it is not well converged at $E_{cut} = 30$ Ry. One might initially think in order to investigate the PTO surface chemistry, an E_{cut} higher than 30 Ry is needed. Obviously one can always use a higher E_{cut} at the expense of increasing computational time, but as Table 4.2 suggests within the range of precision we are looking for, although it is important to use a high E_{cut}



Figure 4.2.1: A sample $c(2\times 2)$ unit cell used in our calculations. Gray balls are Pb, fuchsia balls are O, green balls are H, blue Ti balls are encaged in the blue octahedra formed by the O, and Pt atoms that are used as an electrode at the bottom of the cell are shown in red. Each supercell contains at least 15 Å of vacuum to isolate periodic copies of the slab in the z direction.

structure for 3 fixed layers of PTO, but once this is fixed, it is not important whether we relax the rest of the structure using cutoff energy of 30 Ry or higher. Based on this observation, choosing the structure of our fixed layers to be that of 80 Ry and then relaxing the rest using $E_{cut} = 30$ Ry yields binding energies which have an error of 0.1 eV relative to those that can be calculated in the limit of very high E_{cut} (which is computationally much more expensive).

| PTO structure at different E_{cut} | a | c/a |
|--------------------------------------|------|------|
| 30 Ry | 3.89 | 1.12 |
| 40 Ry | 3.83 | 1.23 |
| 50 Ry | 3.84 | 1.22 |
| 60 Ry | 3.83 | 1.24 |
| 80 Ry | 3.84 | 1.23 |

Table 4.1: Sensitivity of PTO bulk structure to the E_{cut} in plane wave calculations PTO structure at different E_{cut} a c/a

Table 4.2: Sensitivity of binding energies (per adsorbate) to the structure chosen for fixed layers, and free layers on Ti-terminated PTO.

| E _{cut} used for fixed | Energy cost to create 0.5 | |
|---------------------------------|---------------------------|--|
| and free layers | ML O vacancy (eV) | |
| 30 Ry for all layers | 2.6 | |
| 40 Ry for fixed layers | 2.3 | |
| rest relaxed at 30 Ry | 2.0 | |
| 40 Ry for fixed layers | 2.3 | |
| rest relaxed at 40 Ry | 2.0 | |

As can be seen in Fig. 4.2.1, we have used 4 unit cells of PTO stacked in the z-direction per 1×1 surface unit cell. Fig. 4.2.2 shows the projected density of states (PDOS) on the surface Ti atom (on the Ti-terminated surface), which is very well converged at a thickness equal to, or more than 3.5 unit cell of PTO.



Figure 4.2.2: Projected density of states on a surface Ti atom in positively polarized Ti-terminated PTO as a function of number of unit cells of PTO. Electronic structure of the surface is well converged at a thickness of 3.5 unit cell or more.

4.3 Atomic and electronic reconstructions on ferroelectric surfaces

First, we analyze the electronic structure of the bulk PTO, then we compare it to the paraelectric, positive and negatively poled surfaces. In Fig 4.3.1 one can see the valence and conduction bands of the paraelectric surface of PTO. If the surface is Pbterminated, the conduction band edge is Pb 6pl otherwise it is Ti 3d. The paraelectric surface has a bulk-like electronic structure (see Fig. 4.3.2). The Fermi energy (E_F) lies in the gap between the conduction band edge Pb 6p and the valence band edge O 2p states. The main difference between the paraelectric surface electronic structure relative to bulk PTO happens above the Fermi level, in which the Pb 6p_z band shifts lower in energy and gets closer to E_F due to the existence of the surface and removal of a bond from the oxygen atom above (O 2p state whose anti-bonding overlap used to push this Pb 6p_z state higher in energy in the bulk). On the other hand, the surface electronic structure of positive and negatively poled surfaces exhibit major differences with bulk PTO. Ferroelectric materials (e.g., PbTiO₃) possess a switchable



Figure 4.3.1: Valence and conduction bands of bulk PTO.

bulk electrical polarization vector \vec{P} that couples to temperature (pyroelectricity) [183], strain [184, 185, 186], external magnetic [94, 187, 61] and electric fields [188, 189]. When \vec{P} has a non-zero component along the surface normal \hat{n} , so that $\vec{P} \cdot \hat{n} \neq 0$, one has a polar surface [56, 190]. If the surface polarization were uncompensated, a constant electric field would develop in the material that would contribute an energy cost growing linearly with the material thickness, which is untenable for thick samples. Once an equal amount of compensating surface charge appears on the surface (with areal charge density $\sigma = -\vec{P} \cdot \hat{n}$), the interior field is canceled. Consequently, if one controls the direction and/or magnitude of the ferroelectric polarization, the surface properties are modified due to the changing compensation [54, 191, 192, 131, 61].

4.3.1 Electronic reconstructions

The simplest compensation scenario is to accumulate electrons (when $\vec{P} \cdot \hat{n} > 0$) or holes (when $\vec{P} \cdot n < 0$) in the electronic bands of the stoichiometric surface. Figure 4.3.3 shows an example of this for the PbO-terminated (001) stoichiometric surface of PbTiO₃. This is an electronic reconstruction [57, 59, 58, 193, 194, 195].



Figure 4.3.2: Projected density of states(PDOS) on a Pb atom in bulk paraelectric PTO (on left) compared to PDOS on a Pb atom on the surface of the PTO.

We quantified the number of electrons or holes that are doped to the surface by using a projected density of states (PDOS) on the atomic orbitals. In the positive polarization we integrated the states in the conduction band below E_F , while in the negative polarization we integrated the states in the valence band above E_F . Our results show that polarization can shuttle ≈ 1.1 electron per 1 × 1 surface unit cell. This number is based on the PTO bulk polarization calculated using GGA exchangecorrelation functional and by means of the Berry phase method [197, 52], which is $\approx 120 \frac{\mu C}{cm^2}$. The experimental remnant polarization value measured for ferroelectric PZT at room temperature is $\approx 95 \frac{\mu C}{cm^2}$ [181, 182], which corresponds to ≈ 0.9 electron per 1 × 1 surface unit cell. Both our theoretical result and experiment agree that polarization can shuttle ≈ 1 electron per 1 × 1 surface unit; this fact will be frequently used throughout this text to rationalize some of the polarization dependent surface phenomena observed on the ferroelectric surface. Table 4.3 shows the distribution of the doped electrons (holes) close to the surface.



Figure 4.3.3: Reconstructions of the stoichiometric Pb-terminated PbTiO₃ (001) surface. Local density of states at E_F for (a) positive and (b) negative out-of-plane polarization. Pb atoms are gray balls, O magenta, Ti cyan, and the local density of states is in red. In (a), electrons accumulate in the surface conduction bands dominated by Pb 6p orbitals. In (b), holes accumulate in the O 2p-dominated valence bands. (c) Atomic projected density of states for negatively poled surfaces with blue arrows highlighting hole states. Left: electronic reconstruction for primitive (1 × 1) stoichiometric surface unit cell. Center: electronic reconstruction for geometrically reconstructed $c(2 \times 2)$ stoichiometric surface. Right: atomically reconstructed $c(2 \times 2)$ surface with 0.5 ML O vacancies. In going from left to center, the surface breaks symmetry thereby pushing filled states lower in energy and empty (hole) states higher in energy around E_F . On the right, the removal of O atoms creates high energy hole states with strong Pb 6p contributions near the conduction band edge. Part (a) and (b) are rendered using the XCrySDen software [196].

| Distance from surface | Extra electrons in | Extra holes |
|-----------------------|--------------------|---------------|
| | (+)PTO | in (-)PTO |
| 0 atomic layer | 0.917 on Pb | 0.202 on Pb |
| | 0.053 on O | 0.520 on O |
| 1 atomic layer | 0.066 on Ti | 0.026 on Ti |
| | 0.007 on O | 0.090 on O |
| 2 atomic layer | 0.006 on Pb | <=0.001 on Pb |
| | <=0.001 on O | 0.078 on O |
| 3 atomic layer | <-0.001 | <=0.001 on Ti |
| | | 0.027 on O |

Table 4.3: Distribution of extra electrons (holes) on atoms beneath the surface of positively (negatively) polarized PTO (shown by (+)PTO and (-)PTO)

4.3.2 Geometric reconstructions

In addition to the electronic reconstruction, the geometric arrangement of surface atoms may also reconstruct to further stabilize the surface: typically there is a symmetry breaking that pushes bonding states further below and anti-bonding states further above the Fermi level (E_F), similar in spirit to a Peierls distortion [198, 199, 200, 201].

4.3.2.1 Geometric reconstructions on the paraelectric PTO surface

The surface of stoichiometric paraelectric PTO shows geometrical features and symmetry breakings that are absent in the bulk. Figure 4.3.4 shows atomic reconstructions in 1×1 and $c(2\times2)$ cells. Our calculations show that the surface prefers a $c(2\times2)$ over a 1x1 reconstruction by almost 0.2 eV per unit cell. In both cases Pb atoms have moved from the center of neighboring coplanar oxygens. In 1×1 reconstructions oxygen atoms form square cages around the lead; this symmetry is broken in the $c(2\times2)$ cell. As can be seen in Figs. 4.3.4 and 4.3.5, one feature that exists in $c(2\times2)$ but is absent in 1×1 is formation of Pb chains, which are Pb atoms with decreased interatomic distance (3.75 instead of 3.86 Å)



Figure 4.3.4: Geometric reconstructions on the surface of paraelectric Pb-terminated PTO. a) Surface reconstructions on a 1×1 cell, b) surface reconstructions in a $c(2 \times 2)$ cell, where dashed lines show the lead dimers

4.3.2.2 Geometric reconstructions on the negatively-poled PTO surface

The surface of stoichiometric negatively poled PTO shows geometrical features that are absent in the bulk. Figure 4.3.6 shows atomic reconstructions in both 1×1 and $c(2\times2)$ cases. As Fig. 4.3.6 shows, in the 1×1 reconstruction scenario the surface Pb atoms are no longer in their bulk positions (middle of a square made by 4 equidistant coplanar oxygen atoms), as they are almost 0.4 Å closer to two of these oxygens. As Figs. 4.3.6 and 4.3.7 show, in a $c(2\times2)$ reconstruction the surface experiences major reconstructions: one can notice rotation and tilting of the oxygen octahedra in the top layers. The surface displays edge-like reconstructions (in Fig. 4.3.6(c) these edges are perpendicular to the page). Pb atoms tend to dimerize along these edges and the Pb-Pb distance alternates between 3.67 and 3.82 Å. Oxygen atoms also dimerize along the edges and the O-O distance alternates between 3.12 and 3.36 Å. Our calculations show that the surface prefers a $c(2\times2)$ over a 1×1 reconstruction by almost 0.4 eV per unit cell.

Figure 4.3.8 shows how these reconstructions affect the surface electronic structure by reducing the density of states at E_F . One can think of this as forming new bonding



Figure 4.3.5: Geometric reconstructions and formation of dimers on paraelectric Pbterminated PTO. Oxygen is shown by red, Pb is gray and Ti is encaged in oxygen octahedra. At the top a side view of the surface is shown, while a top view can be seen at the bottom. On the right side of the figure, total potential is shown by the help of two dimensional sections at the surface, in which darker color indicates a deeper potential. This clearly shows the formation of dimers on the surface.



Figure 4.3.6: Geometric reconstructions on negatively poled PTO. a) side view in 1×1 cell (top 3 atomic layers is shown, and the surface is the topmost layer), b) top view of the reconstructions in 1×1 cell, c) side view of reconstructions in $c(2 \times 2)$ cell, d) top view of reconstructions in $c(2 \times 2)$ cell.

and antibonding states close to E_F , in which the antibonding states are pushed above the Fermi level and get depopulated, while the bonding states go deeper in energy below Fermi level and get more populated. This leads to stabilization of the surface and is the driving force behind the reconstruction. This mechanism is similar to Peierls distortion, in which a 1 dimensional chain of atoms with a Fermi energy crossing its conduction band breaks symmetry by oscillations in interatomic distances, which leads to opening a gap around E_F and stabilization of the chain [202, 200, 201]. These reconstructions are due to the existence of extra holes on the surface and cause the partially filled valence band to split into two parts, one part fully occupied and the other fully unoccupied (as can be seen in Fig. 4.3.8).

We also relax the negatively polarized surface using a bigger cell (2×2) , but this does not reduce the surface energy any further; hence we think a $c(2\times 2)$ reconstruction is a good model for the stoichiometric positively poled PTO surface that captures the



Figure 4.3.7: Geometric reconstructions and formation of dimers on negatively-poled Pb-terminated PTO. Oxygen is shown by red, Pb is Gray and Ti is encaged in oxygen octahedra. At the top a side view of the surface is shown, while a top view can be seen at the bottom. On the right side of the figure, total potential is shown by the help of two dimensional sections at the surface, in which darker color indicates a deeper potential. This clearly shows the formation of dimers on the surface.



most important geometric reconstructions.

Figure 4.3.8: Projected density of states (PDOS) on the surface O and Pb atoms for a) 1×1 surface reconstruction and b) $c(2 \times 2)$ surface reconstruction. The Pb states that appear just above Fermi level are a hybrid of Pb 6s and Pb 6p states but they mostly consist of Pb 6s states. The character of O 2p states just above the Fermi level changes between O $2p_x$ and O $2p_y$ alternatively as we move along the direction of the edge-like feature .

4.3.2.3 Geometric reconstructions on the positively-poled PTO surface

The positively poled stoichiometric Pb-terminated PTO surface experiences two types of geometric reconstructions: 1) Sliding of the top Pb layer over the surface oxygens by half a unit cell (Figs. 4.3.9 and 4.3.13). 2) Dimerization of the surface Pb atoms (Figures 4.3.12 and 4.3.13). The former lowers the surface energy by about 0.6 eV, while the later lowers it by about 0.1 eV per unit cell.

We begin by studying sliding. The conduction band in Pb terminated PTO is mostly formed by Pb 6p states, while the valence band is mostly consists of O 2p



Figure 4.3.9: A top view of the sliding of the top Pb layer in the x direction by half a lattice constant (along with moving up in the z direction by about 0.5 $\stackrel{\circ}{A}$). Here the green orbitals are Pb 6p_x and 6p_y orbitals and the blue orbitals are O 2p_x and 2p_y orbitals.

states (see Fig. 4.3.1). In the perovskite structure, the conduction Pb 6p band is shifted up in energy (antibonding state) by the valence O 2p band, which itself is pushed down (bonding state). As Fig 4.3.9 shows, sliding of the top Pb atoms in the x direction decreases the interaction (overlap) of Pb 6p_x and O 2p_x orbitals while increasing the overlap of Pb 6p_y and O 2p_y orbitals. This causes Pb 6p_x orbitals to shift lower in energy and O 2p_x to shift higher, while it causes the Pb 6p_y to shift higher and O 2p_y to shift lower (see Fig. 4.3.10). Before sliding, by symmetry there is no difference between Pb 6p_x and Pb 6p_y in the PDOS plots; as can be seen on the left hand side of Fig. 4.3.10 these two bands are overlapping with each other and the center of both is 1.71 eV above E_F , while the center of O 2p_x and O 2p_y, which are also overlapping, is 4.46 eV below E_F . After sliding, the center of Pb 6p_x and Pb 6p_y are accordingly at 1.23 and 2.39 eV higher than E_F , which agrees with the prediction above. The center of O 2p_x and O 2p_y are accordingly at 4.41 and 5.64 eV lower than E_F . We can see that as a result of sliding we have lower energy Pb 6p_x states


Figure 4.3.10: Projected density of states (PDOS) on the surface Pb atom on positively poled PTO. a) without sliding, b) with sliding. One should note in order to make the plot less complicated we only draw the oxygen states which are in the valence band, and only Pb states that are in the conduction band.

below E_F which accommodate extra surface electrons with a lower energy cost. The creation of these lower energy Pb $6p_x$ states and the existence of extra electrons on the surface are the driving force behind the sliding on positively poled PTO. We use the Nudged Elastic Band (NEB) method [20, 19, 203, 18] to calculate the possible barrier for this reconstruction, and it turns out the barrier is negligible (< 0.1 eV per surface unit cell).

Now we turn our attention to the other kind of surface reconstructions, i.e., dimerization of the surface Pb atoms. The main effect of dimerization is to increase the π bonding strength between the Pb 6p_z orbitals of two adjacent Pb atoms, which leads to a broader Pb 6p_z band, and consequently more lower energy Pb 6p_z states below E_F (see Fig 4.3.11). The standard deviations from the center of the band for Pb 6p_z before and after dimerization are calculated to be 1.0 eV and 1.4 eV, respectively.

Figure 4.3.12 shows the integrated local density of states (ILDOS) close to E_F for the surface after both dimerization and sliding of the top Pb layer have taken place. One can notice the formation of "banana bonds" between the adjacent Pb



Figure 4.3.11: Projected density of states (PDOS) on a Pb atom on positively poled PTO. a) on the surface which has experienced "sliding" without dimerization, b) on the surface which has experienced "sliding" with dimerization.

atoms which host the extra electrons on the surface. These "banana bonds" as can be seen in Figures 4.3.11 and 4.3.12 are hybrids of Pb $6p_x$ and $6p_z$ orbitals.

We also relaxed the positively polarized surface using a bigger cell (2×2) , but this did not reduce the surface energy any further; hence we think a $c(2\times 2)$ reconstruction is a good model for the stoichiometric positively poled PTO surface that captures the most important geometric reconstructions.

4.3.3 Atomic reconstructions

In addition to electronic and geometric reconstructions, if there is sufficient time and atomic mobility on the surface, another compensation avenue is opened: atoms (or molecules) can adsorb or desorb from the surface, which is an atomic reconstruction [204, 205, 206, 207, 208, 209, 210, 131]. The change in surface stoichiometry can provide additional surface states (compared to the stoichiometric surface) that are energetically more favorable for electrons/holes to occupy [131].



Figure 4.3.12: Integrated local density of states (ILDOS) close to Fermi energy on the dimerized positively poled $PbTiO_3$ surface. a) 3-dimensional plot showing states close to Fermi energy on both Ti 3d states below the surface and Pb 6p states on the surface. b) 2-dimensional plot in the plane that cuts through the dimerized Pb atoms.

Using DFT, we compute ground state energies for a variety of surface compositions and structures as a function of the ferroelectric polarization. These energies can then be used (following the approach of ref. [54]) to build the phase diagrams [211, 212, 213] shown in Fig. 4.3.14, which describe the most thermodynamically stable surface phases of (001) PbTiO₃ as a function of polarization and Pb and O chemical potentials. The positively polarized PbTiO₃ surface prefers to have 0.5 ML of Pb vacancies, whereas the negatively poled prefers 0.5 ML of oxygen vacancies; in comparison, the non-polar paraelectric PbTiO₃ surface prefers to have stoichiometric termination. (In all cases, the surfaces prefer to be Pb- instead of Ti-terminated, which is in agreement with the literature [214, 215, 216].) The densities of states plot in Fig. 4.3.3(c) explains why negatively poled PbTiO₃ prefers to atomically reconstruct: when oxygen vacancies form on the surface, high energy (Pb 6p dominated) surface states appear in the spectrum, and these states happily accommodate the compensating holes, lower the total energy and lead to greater chemical stability. In addition, O vacancy formation pushes down the center of the O 2p surface valence



Figure 4.3.13: Geometric reconstructions and formation of dimers on positively-poled Pb-terminated PTO. Oxygen is shown by red, Pb is Gray and Ti is encaged in oxygen octahedra. At the top a side view of the surface is shown, while a top view can be seen at the bottom. On the right side of the figure, total potential is shown by the help of two dimensional sections at the surface, in which darker color indicates a deeper potential. This clearly shows the formation of dimers on the surface.



band relative to E_F by ≈ 0.45 eV which further enhances stability [30, 61].

Figure 4.3.14: Phase diagrams for the (001) surfaces of negatively polarized, paraelectric and positively polarized PbTiO₃. Each colored region shows the most thermodynamically stable state as a function of O and Pb chemical potentials. The physically allowed region within which PbTiO₃ is stable (against decomposition into various combinations of compounds made of Pb, Ti and O) is within the dashed trapezoid.

4.4 Thermodynamically stable phases of $PbTiO_3$ in a mixed O_2 and H_2O atmosphere

With the above fundamentals in mind, we examine the thermodynamics of PbTiO₃ surfaces in a mixed H₂O and O₂ atmosphere. First, we build surface phase diagrams as a function of H₂O and O₂ chemical potentials. As shown in Fig. 4.4.1, under easily accessible ranges of chemical potentials ($-1 eV \leq \mu_{H_2O}$, $\mu_O \leq 0 eV$), i.e., pressures above 10^{-4} atm and temperatures below 450 °C [217], the thermodynamically stable surface of (i) negatively poled PbTiO₃ is covered with 1 ML of H chemisorbed to surface O atoms forming OH⁻, (ii) the paraelectric surface remains stoichiometric with possible weak physisorption of H₂O and O₂, and (iii) positively poled PbTiO₃ is covered with 1 ML OH which is chemisorbed to the surface Pb forming OH⁻.

These findings are readily understood based on charge counting and the fact that the magnitude $|\vec{P}|$ of the bulk polarization of PbTiO₃ corresponds to ≈ 1 fundamental



Figure 4.4.1: Polarization-dependent phase diagrams of Pb-terminated (001) PbTiO₃ surfaces as a function of H₂O and O chemical potentials μ_{H_2O} and μ_O . Each colored and labeled region represents the most stable thermodynamic phase. In the most relevant range of chemical potentials ($-1 eV \leq \mu_{H_2O}, \mu_O \leq 0 eV$) the negatively-poled surface prefers to be covered with 1 ML of H, the paraelectric surface prefers to be stoichiometric, and the positively-poled surface has 1 ML OH.

unit of charge per primitive 1×1 surface unit cell (s.u.c.) [182, 181, 61]. Within an ionic picture, each PbO plane in the bulk-like regions of PbTiO₃ consists of Pb²⁺ cations and O²⁻ anions. The stoichiometric negatively-poled surface is compensated by ≈ 1 hole per s.u.c. that resides primarily in the O 2p surface states of oxygen anions (making them O⁻): having one H bound to each surface O anion leads to the formation of 1 ML OH⁻ and the hole happily moves to the H 1s dominated antibonding state of the O-H bond. For the stoichiometric positively-poled surface, the compensating electron resides mainly in the Pb 6p states of Pb cations (making them Pb⁺): when an OH binds to each surface Pb cation, the electron favorably fills the low-energy available bonding state of the OH to form OH⁻ (and the Pb become Pb²⁺ again). The stoichiometric paraelectric surface is insulating, has no excess holes or electrons, and lacks any interest in forming chemical bonds.

4.5 Water splitting by cyclic polarization modulation

These phase diagrams can be used to design a cyclic catalytic pathway for water splitting. By cyclically switching the ferroelectric polarization, one can leverage the differences in preferred thermodynamic surface phases of the different polarizations to drive forth desired reactions. In the present case, cycling between the paraelectric and negative surfaces suggests the following intriguing scenario. Starting with the negatively poled surface, it quickly reconstructs to form 0.5 ML of O vacancies (which is the thermodynamic ground state in the absence of H₂O molecules). Next, 0.5 ML H₂O will readily dissociate to form chemisorbed H and OH (with the OH filling the 0.5 ML O vacancies) leading to a surface covered with atomic H (the thermodynamic ground state for negative polarization in a mixed O₂ and H₂O atmosphere). When the ferroelectric enters the paraelectric phase (e.g., via an increase in temperature), the H atoms can recombine to form H₂ which will then desorb to leave a pristine stoichiometric surface (the preferred state for the paraelectric case). This cycle can then be repeated.

We verify the feasibility of this scenario by computing key energy barriers via the nudged elastic band (NEB) [18, 19, 21, 20] and constrained relaxation [218, 219] methods. The barriers turn out to be favorable, and the cycle and its energy landscape are depicted in Fig. 4.5.1. We now explain the key labeled steps I-X. We begin in step I with a pristine negatively-poled surface compensated by ≈ 1 hole per s.u.c. The surface prefers to atomically reconstruct (steps II-III) whereby half of the surface O combine to form weakly bound O₂ molecules that leave the surface. The energy barrier for this process is only 0.4 eV per O₂ molecule so the surface should atomically reconstruct rapidly to its preferred 0.5 ML vacancy structure, especially since no molecular binding or dissociation is required [54]. However, once H₂O molecules are



Figure 4.5.1: Water splitting $(2H_2O \rightarrow O_2 + 2H_2)$ by cyclic switching between the negatively-poled and paraelectric surfaces of (001) PbTiO₃. (a) depicts the cycle. In brief, two H₂O molecules are dissociated on negatively poled surface to produce bound atomic H; when the surface is switched to the paraelectric phase, the H atoms recombine to form weakly bound H₂ making for a pristine surface ready for the next cycle. See the text for further details. (b) shows the energy landscape for the cycle and includes meta stable states (solid line segments) and transition states (circles connected by dotted lines). The oxygen formation barrier (between step I and II) is 0.4 eV, and the hydrogen formation energy (between step VI and VII, and also step VIII and IX) is 0.3 eV.

present and adsorb, the system prefers a new thermodynamic state. We find that the H_2O molecules dissociate into bound H and OH barrierlessly on this vacancy rich surface (steps III-V): the surface ends up with 1 ML H chemisorbed on a stoichiometric PbO layer. The surface is now passivated by the strongly bound H atoms and is chemically inactive.

Next, we move the system to the paraelectric phase (e.g., by increasing the temperature above the Curie temperature T_c of the ferroelectric). Now, having 1 ML of H on the surface (step VI) is far from the ground state of the paraelectric surface: it prefers to be stoichiometric and have weakly physisorbed H₂ molecules. We find a small barrier of 0.3 eV for H₂ formation (steps VII-IX). Once the paraelectric surface reaches this final state (step X), it is in its ground state and chemically inert, and the H₂ molecules can leave the surface easily. We can repeat this cycle anew by returning to the negatively-poled surface (steps X-I), e.g., by lowering the temperature below T_c. In short, we propose to use temperature, via the pyroelectric effect, as a switch that controls the substrate's ferroelectric order. By modulating the temperature cyclically, we periodically push the system out of equilibrium then leverage the surface's tendency to reach its thermodynamic ground state to drive desired parts of the water splitting reaction.

The absolute energies computed by DFT (GGA-PW91 XC) for structures and molecules that are involved in this catalytic cycle are given in the Table 4.4. Also, Table 4.5 contains the important energy barriers involved in this catalytic cycle.

As mentioned by Kalinin et al. [221], when the polarization screening on ferroelectric surfaces is due to charged adsorbates, the relaxation (desorption) of these charges can be a potentially slow process. Luckily, in our system, the relaxation should be fast: e.g., when the system covered by 1 ML H is switched from negative to paraelectric phase, the H₂ formation barrier is quite small at 0.3 eV and the H₂ molecules are only weakly physisorbed.

We note that, in principle, an alternative pathway for the negatively polarized surface to reach its most stable thermodynamic state (1 ML H chemisorbed) is to dissociate H_2 molecules on the starting (out of equilibrium) stoichiometric surface. The H_2 dissociation barrier is calculated to be 0.6 eV on this surface, which is higher



Figure 4.5.2: Key structures during (a-b) H_2O dissociation on the vacancy rich (0.5 ML O vacancy) negatively-poled PbTiO₃ (001) surface and (b-c) H_2 production on the paraelectric surface. Gray balls are Pb, fuchsia balls are O, green balls are H, and blue Ti balls are encaged in the blue octahedra formed by the O. Each surface O vacancy makes for an octahedron with missing apex in (a). In (a), H_2O molecules are above the negatively-poled surface. Each water molecule splits into H and OH barrierlessly: the H binds to the surface O and the OH fills the O vacancy to produce the thermodynamic ground state in (b) sporting 1 ML chemisorbed H. (c) shows the ground state of the paraelectric surface: the H atoms from (b) form H_2 molecules with a small barrier of 0.3 eV and are weakly physisorbed to this stoichiometric surface. This figure is rendered using VESTA [220].

than 0.4 eV barrier for O_2 formation (which creates 0.5 ML oxygen vacancy on the surface) and 0.0 eV barrier for H_2O dissociation (on the surface with 0.5 ML oxygen vacancies) which brings the surface to its thermodynamic ground state. Thus the preferred pathway for the negatively poled surface to reach its thermodynamic ground state is via H_2O dissociation as opposed to H_2 dissociation. Therefore, the H_2 molecules produced in this scheme in the paraelectric phase do not dissociate back to atomic hydrogen upon entering negative polarization and can accumulate and be extracted from the cycle.

Finally, a different possible pathway is that H_2 molecules reduce the negatively polarized surface, form H_2O and leave the surface with oxygen vacancies. This turns out to be both thermodynamically and kinetically prohibited. Thermodynamically, the surface phase that includes atomic H is more favorable (by 0.8 eV per H_2 molecule) than H_2O physisorbed on the surface with oxygen vacancies. Kinetically, this reac-

| Structure, atom or molecule | Total Energy (Ry) |
|---|-------------------|
| Bare negatively poled PTO surface (2×2) | -7491.2091 |
| Transition state of O_2 forming on neg. surface (2×2) | -7491.1814 |
| Negatively poled PTO surface with 0.5 ML O vac. $c(2 \times 2)$ | -3713.679 |
| Negatively poled PTO surface with 0.5 ML O vac. (2×2) | -7427.3283 |
| O_2 on negatively poled PTO with 0.5 ML O vac. (2×2) | -7491.3000 |
| Negatively poled PTO surface with 1 ML H $c(2 \times 2)$ | -3748.2853 |
| Paraelectric PTO surface with 1 ML H $c(2 \times 2)$ | -3748.0499 |
| Transition state of H_2 forming on paraelectric surface $c(2 \times 2)$ | -3748.0292 |
| H_2 on paraelectric surface $c(2 \times 2)$ | -3748.1010 |
| Bare paraelectric surface $c(2 \times 2)$ | -3745.7603 |
| H_2 (in a big box, i.e., in gas) | -2.3377 |
| H (in a big box, i.e., in gas) | -0.9202 |
| O_2 (in a big box, i.e., in gas) | -63.9792 |
| OH (in a big box, i.e., in gas) | -33.0628 |
| H_2O (in a big box, i.e., in gas) | -34.5066 |

Table 4.4: The absolute energies computed by DFT (GGA-PW91 XC) for structures and molecules that are involved in the catalytic water splitting cycle.

Table 4.5: Important energy barriers involved in the water splitting catalytic cycle.

| Process | Energy Barrier (eV) |
|---|---------------------|
| O ₂ formation barrier on negatively poled surface | 0.4 |
| H_2O dissociation on negatively poled 0.5 ML O vac. surface | 0.0 |
| H_2 formation barrier on paraelectric surface | 0.3 |
| O_2 desorption barrier from 0.5 ML O vac. surface | 0.0 |
| H_2 desorption from paraelectric surface | 0.0 |

tion requires H_2 to dissociate and react with surface oxygen to form H_2O which, as mentioned above, has a 0.6 eV barrier per molecule that is higher than the 0.4 eV required for O_2 desorption and 0.0 eV required for H_2O dissociation on the oxygen deficient surface.

4.6 The effect of positively polarized domains

We note that as per Fig. 4.4.1 the positively-poled surface prefers to have 1 ML OH chemisorbed to the surface Pb. We find that the most kinetically favorable pathway for the stoichiometric positively-poled $PbTiO_3$ surface to reach its ground state (1 ML



Figure 4.6.1: Phase diagrams for the positively polarized (001) PbTiO₃ surface for three different Pb chemical potentials. Left: the lowest possible physically allowed value of -2.6 eV as per Fig. 4.3.14. Center: an intermediate Pb chemical potential of -1.3 eV. Right: the highest physically allowed value of 0 eV. Regardless of the Pb chemical potential, the top right corner of the phase diagrams, which corresponds to high enough and reasonable partial pressures of oxygen and water, is dominated by a phase that does not favor Pb vacancies.

of chemisorbed OH) is to first dissociate O_2 molecules into O atoms (a barrierless process) to reach the configuration with 0.5 ML chemisorbed O, and then H₂O molecules barrierlessly dissociate on this surface to bring it to its thermodynamic ground state with 1 ML chemisorbed OH. Hence, although the positively-poled surface can dissociate H₂O, it is not useful for achieving the overall splitting process in our cyclic scheme: the positively poled surface is oxygen rich, and upon being switched to the paraelectric phase, water molecules reform on the surface with no net H₂ production. Thus, while the positive polarization is not useful for water splitting, it does not deter it either. Therefore, our simple recommendation for experimental realization of our cycle is to create and use ferroelectric samples dominated by negatively-poled domains. However, even if the surface ends up with a domain structure [222, 223] having equal amounts of positive and negative polarization, half of the surface will be still active for hydrogen production (and the other half will be inert).

A separate potential concern with the positively-poled surface regards its stoichiometry. As shown in Fig. 4.3.14, if only O_2 is available to the surface, the most thermodynamically favorable surface phase has 0.5 ML Pb vacancies. In contrast,

the negatively polarized and paraelectric surfaces do not favor Pb vacancies. Thus, in principle, it might be possible that the presence of surface Pb vacancies will pin the polarization [224] into the inert positive direction upon cooling below the Curie temperature T_c (if the Pb vacancies do not easily diffuse into the bulk). Thus, for our cyclic scheme to run at full efficiency, one should minimize the concentration of Pb vacancies on the surface. In order to guide future experiments, we build phase diagrams for positively poled $PbTiO_3$ with varying H_2O and O chemical potentials (i.e., for a mixed O_2 and H_2O atmosphere) in which we include surfaces with Pb vacancies. The Pb chemical potential can vary in the physically allowed range of $-2.6 eV \le \mu_{Pb} \le 0 eV$ based on Fig. 4.3.14. (The phase diagram shown in Fig. 4.4.1) for the positively polarized surface was based on an intermediate value of the Pb chemical potential $\mu_{Pb} = -1.3 \, eV$). In Fig. 4.6.1 we show the phase diagrams for the positively polarized surface for three different Pb chemical potential values. It can be seen that even in the extreme case of the lowest possible allowed Pb chemical potential (μ_{Pb} = -2.6 eV), which most strongly favors the formation of Pb vacancies, for reasonable values of the O and H₂O chemical potentials $(-1 eV \le \mu_{H_2O}, \mu_O \le 0 eV)$ the most stable thermodynamic states do not have Pb vacancies. Hence, our recommendation to experimenters is to always keep the $PbTiO_3$ sample in a mixed H_2O and O_2 atmosphere with high enough partial pressures to prevent appearance of Pb vacancies on the surface. Vacuum conditions may be a poor choice when attempting to realize our proposed catalytic cycle for hydrogen production on $PbTiO_3$ or other similar ferroelectrics.

4.7 Operating the catalytic cycle below the Curie temperature

Up to this point, our proposed catalytic cycle relies on using the different properties of the negatively-poled and paraelectric surfaces in tandem via cyclic temperature modulation. We now explain that it is not necessary to drive the system into the fully paraelectric phase: one only needs to make the polarization magnitude small enough to change the thermodynamic ground state of the less polarized surface. Fig. 4.7.1 shows how the surface phase diagram of the negatively-poled surface depends on the out-of-plane component P of the substrate ferroelectric polarization over the wide range of $-120.9 \le P \le 0 \frac{\mu C}{cm^2}$.

The most negative value is determined by the exchange correlation (XC) functional we have used (GGA-PW91) which predicts a bulk polarization magnitude equal to 120.9 $\frac{\mu C}{cm^2}$ for the tetragonal ferroelectric ground state of bulk PbTiO₃ (computed via the Berry phase method [53, 52]). In fact, the magnitude predicted by the GGA-PW91 XC functional is overestimated compared to the experimental value [181, 182] of $\approx 90 \frac{\mu C}{cm^2}$, so we believe the range of values considered in Fig. 4.7.1 encompasses all potentially interesting and accessible polarization magnitudes. Furthermore, for reasonable ranges of oxygen and water chemical potentials ($-1 eV \leq \mu_{H_2O}$, $\mu_O \leq 0 eV$ which correspond to temperatures below 450 °C and pressures above 10^{-4} atm), the stable surface phase with 1 ML H does not change for $P \leq -90 \frac{\mu C}{cm^2}$ so the overestimation is also of no great consequence for physical predictions.

Our key practical conclusion from the data in Fig. 4.7.1 is that one does not actually have to go above the Curie temperature (T_c) and have a fully paraelectric surface in order to "clean off" the atomic H from the surface via production of H₂: as long as the polarization becomes small enough (roughly below 20 $\frac{\mu C}{cm^2}$ in magnitude), the surface still prefers to be stoichiometric, so atomic H will leave the surface in the



Figure 4.7.1: Surface phase diagrams of the negatively-poled PbTiO₃ surface as a function of the (fixed) magnitude of the substrate out-of-plane polarization within the range of $-120.9 \leq P_z \leq 0 \frac{\mu C}{cm^2}$. For simplicity of presentation, when creating these diagrams we have only included phases with chemisorbed species and have excluded phases that have additional weakly physisorbed molecules.

form of H₂ molecules. Figure 4.7.1 also illustrates that a hydrogen production cycle is most efficient if $P \leq -70 \frac{\mu C}{cm^2}$ in the low temperature part of the cycle: polarizations of $-70 \leq P \leq -40 \frac{\mu C}{cm^2}$ will still dissociate water to create bound H atoms, but with a lower efficiency because the preferred coverage is only 0.5 ML H (instead of 1 ML H for larger polarization magnitudes). In brief, while the maximum theoretical catalytic efficiency occurs by cycling between fully paraelectric and negatively-poled surfaces, a smaller change of polarization can be sufficient to drive the catalytic cycle, albeit with somewhat reduced efficiency, which translates into a smaller required temperature modulation.

We end this section by noting that the coupling between polarization and temperature (pyroelectricity) is only one way to cycle the ferroelectric surface between the large-magnitude and small-magnitude polarization regimes. Another avenue is to use the coupling between polarization and strain (piezoelectricity) [128], or polarization and electric/magnetic fields, alone or in tandem with pyroelectricity.

4.8 Effect of the exchange-correlation (XC) functional on surface phase diagrams

The energies reported above use the GGA-PW91 exchange-correlation (XC) functional [13, 14]. In order to check the potential dependence of our key results on the choice of XC functional, we compute surface phase diagrams for three different choices of XC functionals. The resulting surface diagrams are shown in Fig. 4.8.1. As can be seen in the first row of Fig. 4.8.1, LDA-PZ [12], GGA-PBE [14] and GGA-PW91 all predict a stoichiometric phase for the paraelectric surface for reasonably accessible ranges of oxygen and water chemical potentials $(-1 eV \leq \mu_{H_2O}, \mu_O \leq 0 eV)$. For a negatively polarized substrate where the magnitude of the out-of-plane polarization in the bulk-like regions of the substrate is fixed to the experimentally observed magnitude of $P \approx 90 \frac{\mu C}{cm^2}$ (2nd row of the figure), all three XC functionals predict very similar phase diagrams. This means that, for a fixed polarization, the different XC approximations do not predict strongly differing binding energies to the surface. In the 3rd row of Fig. 4.8.1, we see that the phase diagram that the LDA-PZ XC functional predicts is different from the GGA XC functionals. The root cause of this difference is that the bulk ferroelectric polarization magnitudes differ between the functionals: the GGAs overestimate $(P \approx 120 \frac{\mu C}{cm^2})$ while LDA underestimates $(P \approx 60 \frac{\mu C}{cm^2})$. Hence, the main determinant of the nature of the phase diagram is the magnitude of the bulk ferroelectric polarization (which should be well reproduced by the theoretical approach or should be fixed "by hand"); the actual binding energies to the surfaces are far less sensitive to the choice of XC functional.



Figure 4.8.1: Surface phase diagrams calculated for paraelectric (1st row) and negatively polarized (2nd and 3rd row) (001) PbTiO₃ substrates using different exchangecorrelation (XC) functionals: LDA-PZ (1st column), GGA-PBE (2nd column) and GGA-PW91 (3rd column). The phase diagrams in the 3rd row are based on fully relaxed calculations for negative polarization, while the phase diagrams in the 2nd row are based on calculations in which the interior atomic layers of the ferroelectric are fixed to produce a specific polarization of $P \approx 90 \frac{\mu C}{cm^2}$ but the surface layer is free to relax. Comparing the second and third row isolates the XC-dependent effect of the bulk polarization as opposed to the pure XC-dependence of the surface binding energies.

4.9 Conclusion

In conclusion, we propose a catalytic cycle (schematically shown in Fig. 4.9.1) for water splitting in which we exploit the different electronic properties and thermodynamic ground states of the negatively-poled and paraelectric surfaces of a ferroelectric oxide. By using the pyroelectric effect, one is able to switch the ferroelectric into (and back from) its paraelectric phase by modulating the temperature near the ferroelectric Curie temperature T_c . Luckily, the T_c for workhorse ferroelectrics such as $PbZr_xTi_{1-x}O_3$ and $BaTiO_3$ solid solutions can be tuned in the useful range of 100 - $450^{\circ}C$ [157, 158]. Hence, in practice, the energy needed to drive this cycle may be provided by low/intermediate grade heat sources: e.g., geothermal sources, industrial waste heat or concentrated solar power. In addition, as no precious metals are required in this approach, one can envisage using earth abundant elements to create viable water splitting catalysts.

A device that operates based on our proposed catalytic cycle, can: a) be very small in size (thin ferroelectric films), b) can run on waste heat or concentrated solar energy, and c) can operate in reasonable ranges of temperature and pressure. These properties may make such a device useful in a decentralized catalysis scheme [225, 226], where useful chemicals can be produced for personal use or for small communities locally and on demand. Such a scenario can be favorable, not only because one can put waste energy into use, but also in the sense that one can save expenses associated with transportation and large scale storage of chemicals.



Figure 4.9.1: Schematic outline of the water splitting cycle exploiting the pyroelectric properties of ferroelectric oxides.

Chapter 5

NO_x direct decomposition on ferroelectrics

5.1 Introduction

 NO_x is the generic term for the nitrogen oxides NO and NO_2 . They are produced from the reaction between nitrogen and oxygen at high temperatures (e.g., in a car engine). In areas of high motor vehicle traffic, such as in large cities, the amount of nitrogen oxides emitted into the atmosphere as air pollution can be significant. NO_x can react in the atmosphere to form acid rain. Thus environmental regulations are pushing for a sharp decrease in NO_x emission. The current technologies implemented in automotive industries mostly use three-way catalytic converters (TWC) to reduce NO_x to N_2 and O_2 [227], in which unburnt hydrocarbons and CO are oxidized and NO_x molecules are reduced to N_2 and O_2 . The limitation of this method is that in order to prevent the catalyst from being poisoned by oxygen one needs unburnt hydrocarbons and CO in the gas intake, which implies that the engine should operate with a stoichiometric fuel to air ratio, and not in an oxygen rich environment (lean burn) which would yield a higher energy efficiency and less CO₂ emission per energy unit extracted from the fuel. A NO_x direct reduction (decomposition) catalyst that can operate in a higher oxygen pressure environment has been a long standing goal in the automotive industry [227, 228]. We show that using the polarization of PbTiO₃ as a switch we can greatly affect the surface chemistry and binding energies, paving the road for designing a NO_x direct reduction catalyst, especially by overcoming the problem of oxygen inhibition (poisoning) [229, 230, 231, 232].

5.2 Atomic and electronically reconstructed ferroelectric surfaces

An important question for one who intends to investigate $PbTiO_3$ (PTO) surface chemistry is which kind of surfaces should one consider: stoichiometric surfaces that are only electronically and geometrically reconstructed, or surfaces that have undergone non-stoichiometric atomic reconstructions? There is no unique answer to this question. It depends on what one tries to simulate. If one is interested in the steady state behavior of a ferroelectric surface, then the surface with non-stoichiometric atomic reconstructions should be studied. But in this chapter (although we will investigate this steady state behavior in one section) the main focus is to study the properties of stoichiometric surfaces. The reason for this as explained in the previous chapter is that we are interested in designing a catalyst that can be actively and alternatively pushed to strong adsorption and strong desorption regimes by cyclically switching the polarization. As explained in Fig. 5.2.1 and based on the difference in time scales for stoichiometric (electronic and geometric) and non-stoichiometric reconstructions, such a cyclic system spends some of its time in a configuration that resembles the stoichiometric surface, which is only electronically and geometrically reconstructed. As was pointed out in our previous work on the PTO surface [54], the most interesting polarization dependent chemistry is seen on such a transient



Figure 5.2.1: A cyclic scheme in which the polarization direction (shown by thick black arrows in up or down direction) is periodically switched. Orange area shows part of the cycle that is positively poled, and blue shows the part that is negatively poled. The top and bottom surfaces are the most thermodynamically stable (atomically reconstructed) PTO surfaces in respectively positive (up) and negative (down) polarizations. The horizontal double arrows show part of the cycle that is much faster than parts designated with single horizontal arrow (because of extreme instability of the configuration in the tail of the arrow in that specific polarization).

state surface: indeed this is the reason why we cyclically switch between the two polarizations.

5.3 Molecules on the stoichiometric Pb terminated PbTiO₃ surface

5.3.1 NO intact molecular binding

NO binding energies and geometries show significant polarization dependence (see Table 5.1 and Fig. 5.3.1). In negative polarization NO is bound to a surface oxygen and forms a NO₂ molecule attached to the surface (Fig 5.3.1). In 0.5 ML coverage (in which half of the oxygens on the surface bind to NO molecules), the effect of this binding is to drag these oxygen atoms by almost 0.9 Å out of the surface upon forming NO₂. The $\angle ONO$ angle in this geometry is 117.6°, the NO bond length between N and the surface O is 1.29 Å, and the bond length of N to the O which

originally belongs to NO molecule is 1.23 Å. One can compare these numbers with the bond angle and bond length of gas phase NO_2 molecule and also the bond length of NO which we have calculated using DFT to be accordingly 133.5°, 1.21 and 1.17 ${
m \ddot{A}}$ (in good agreement with both theoretical and experimental work in the literature [233, 234, 235] keeping in mind that GGA XC functionals overestimate the bond length). One notices that in this structure the $\angle ONO$ bond angle is smaller relative to the gas phase NO₂ molecule and is closer to the bond angle in $(NO_2)^-$ which is 115.4° according to the literature. The NO bond length is also longer than both bond lengths in NO and NO₂ molecules and is closer to the bond length in $(NO_2)^-$ which is reported to be 1.24 \AA [236]. The reason for this will be more evident below, in which we will show there is an electron transfer from the rest of the surface to this formed NO₂ molecule, and we actually have $(NO_2)^{-\delta}$ ($\delta \approx 0.4$) bound to the surface. NO binding to the negatively poled surface is also interesting from the magnetic point of view: it has a quenched magnetic moment of 0.5 $\mu_{\rm B}$ per NO molecule compared to the 1 $\mu_{\rm B}$ magnetic moment of both NO and NO₂ molecules in the gas phase. The reason for this will also be illustrated later by investigating the electronic structure of the surface and the adsorbates.

In positive polarization, NO bridges between two adjacent Pb atoms (Fig. 5.3.1). The attached NO molecule is stretched relative to NO in vacuum, and the interatomic distance is increased by 0.16 Å from 1.17 to 1.33 Å, which is the direct consequence of electron transfer from the surface Pb atoms to the antibonding SOMO of the attached NO molecule.

In the paraelectric case, the NO molecule simply hovers over the surface with a small binding energy (0.3 eV). In this case we have a physisorbed molecule on the surface. One should note that a weak physisorption is indeed expected due to the insulating nature of paraelectric PTO surface that lacks a density of states at the Fermi energy and thus is mostly inert towards adsorbates.

Table 5.1: NO binding energies and geometries as a function of PTO polarization (the coverage is 0.5ML NO, .i.e., 0.5 NO molecule per 1×1 surface unit cell). The binding energy in the negative polarization marked by (*) should be interpreted with caution as here we actually have a NO₂ molecule formed which is weakly bound to rest of the surface (with 0.5 ML O vacancy)

| Polarization | binding geometry | binding energy(eV) |
|--------------|---------------------|--------------------|
| positive | NO bridges Pb sites | 1.5 |
| paraelectric | physisorption | 0.3 |
| negative | NO_2 forms | 1.9* |



Figure 5.3.1: Comparison of the two binding geometries of NO molecule to PbO terminated PTO (0.5 ML coverage) on a) positively polarized surface and b) on negatively poled surface. Nitrogen is shown in pale blue, O (red), Pb (gray) and Ti is encaged in oxygen octahedra.

Now one might wonder why the binding geometries and binding energies are a function of polarization. In order to answer this question, we study electronic structure of the surfaces and the NO molecule. We begin by analyzing NO binding to the positively poled PTO. In Fig. 5.3.2(a) one can see the Singly Occupied Molecular Orbital (SOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of NO. NO SOMO has π_{2p}^* character, and it is in channel up of spin, while the LUMO has the same character but in channel down of spin. Both NO SOMO and LUMO are mainly localized on the nitrogen atom. This explains our observation that the NO molecule always binds from the N side rather than O side to the PTO surface. The fact that

NO binds from the N side to transition metal and oxide surfaces is also shown in the literature [237, 238, 239, 240, 241, 242].



Figure 5.3.2: SOMO, HOMO and LUMO in different molecules. Red shows positive and blue shows negative regions of the wave function. a) NO: doubly degenerate antibonding state (π_{2p}^*) , SOMO in spin up and LUMO in spin down channel. b) NO₂: antibonding state, HOMO in spin up, LUMO in spin down c) O₂: doubly degenerate antibonding state (π_{2p}^*) , HOMO in spin up LUMO in spin down channel d) N₂ HOMO (σ_{2p}) (e) doubly degenerate N₂ LUMO (π_{2p}^*)

In Fig. 5.3.3 one can see the projected density of the states (PDOS) on the surface Pb atom before and after 0.5 ML NO adsorption. It can be seen why NO binding to the Pb atom on the surface of positively poled PTO leads to a considerable stabilization (1.5 eV per molecule), as both the NO SOMO and LUMO are below E_F of the positively polarized PTO surface respectively by 1.54 eV and 0.19 eV. In addition to significant electron transfer, there will be a covalent binding between the Pb 6p

states whose center is computed to lie above E_F of the surface at $E - E_F = 1.94$ eV and the NO LUMO and SOMO which are located at E - $E_{\rm F}$ = -0.19 eV, E - $E_{\rm F}$ = -1.54 eV, respectively. This covalent interaction creates new low energy bonding states on the surface which have mostly NO π_{2p}^* character and lie below E_F ; it also leads to creation of antibonding states which have mostly Pb 6p character and lie above $E_{\rm F}$. Consequently, the center of Pb 6p band is expected to be pushed up. Fig 5.3.3(b)shows the PDOS on a Pb surface atom after NO adsorption in 0.5 ML coverage, the center of Pb 6p band is confirmed to be pushed up by 0.9 eV. The fact that the center of the Pb 6p band has moved up in energy decreases the interaction of this band with further NO molecules that will attach to this surface. Also the decreased density of states below the Fermi energy leads to lower electron transfer. Both of these lead to a lower binding energy per molecule for higher coverages. We have actually confirmed this prediction by computing the binding energy the for NO molecule in 1 ML coverage, which is 0.9 eV per NO molecule (0.6 eV lower than its value in 0.5 ML coverage). The adsorbates self poisoning effect has been addressed similarly in the literature by considering surface band mediated interactions and density of states near the Fermi energy [243, 244, 245, 246].

We have also computed the real space electron density transfer upon adsorption of 0.5 ML NO molecules, which is shown in Fig. 5.3.4. It can be seen that electrons populate the NO π_{2p}^* states, but are depopulated from regions close to Pb atoms which are adjacent to the N end of the molecule, and also from the Pb dimers (Pb atoms 3.24 Å apart from each other) which are adjacent to its O end. This charge transfer to the NO molecule can also be seen by looking at the Lowdin charges [247] on the NO molecule before and after adsorption to the positively polarized PTO surface, this shows an increase of almost 0.8 e per molecule. One last point to note is the increase in interatomic distance (stretching) of NO molecule upon binding by 0.16 Å, which is a result of the transfer of about 0.8 electron to antibonding NO π_{2p}^* states which



Figure 5.3.3: PDOS on surface Pb atom in positively poled PTO a) before, b) after adsorption of 0.5 ML NO.

causes the molecule to stretch.

Now we turn our attention to the negatively polarized PTO surface. Figure 5.3.5 shows the PDOS on the surface oxygen before and after NO adsorption. In Fig. 5.3.5(a) one notices that E_F for the NO molecule is slightly below E_F of the clean negatively poled surface by 0.19 eV; this should be compared with the case of the NO molecule on positively poled surface (Fig. 5.3.3), in which the NO SOMO is 1.54 eV lower than the E_F of the surface. Hence, unlike the positive polarization case, one would not predict a sizable electron transfer to the NO molecule. Instead one predicts a strong interaction between NO SOMO and center of O 2p band which lies 1 eV below it, and is also partially filled; this creates filled bonding states below and empty antibonding states above E_F which leads to stabilization of the bonding. Also, the NO LUMO further pushes down the partially filled surface O 2p states which will



Figure 5.3.4: Electron density transfer in real space after adsorption of 0.5 ML NO on positively poled PTO: a) top b) side view. Color blue shows electron loss, red electron gain.

also help the stabilization of the NO bond to the surface O atom.

Based on the arguments above one predicts a large binding energy between the NO molecule and stoichiometric negatively poled PTO surface (we have confirmed this numerically as shown in Table 5.1). One should note that at this coverage there are two types of surface oxygens (see Fig. 5.3.1(a)): the first type has an NO molecule attached to it, while the second kind has no molecules attached to it. By looking at the PDOS on this type of oxygen (Fig5.3.5(b)) we can determine the coverage dependence in this polarization. Here the O 2p band has less density of states at E_F after NO adsorption relative to the case before adsorption. We count the number of holes in the O 2p band by integrating the portion of the band above E_F , and it turns out that adsorption of 0.5 ML NO molecule decreases the number of holes on this oxygen atom from 0.48 to 0.19, which might make one think that, like the case of the NO adsorption on positively poled PTO, the binding energy of NO for a higher coverage (1 ML) decreases following the reasoning mentioned in the paper by Feibelman et al (based on the density of states at Fermi energy) [243]. But here,

unlike the positive polarization case, bonding has mostly covalent nature, as opposed to charge transfer. Thus it is the center of the O 2p band that dictates the coverage dependence and not the density of states at E_F . We have calculated the center of the O 2p band (on the first type of oxygen) to be at E = -1.17 eV after NO adsorption, which is exactly the same as before adsorption. This justifies our observation that the NO binding energy remains the same for 1 ML coverage (1.9 eV per NO molecule).

Now we turn our attention to the second type of oxygen atoms after adsorption of 0.5 ML of NO molecules. As Fig. 5.3.5(c) shows, here the O 2p band experiences striking changes. There are many new features and spikes that do not exist before adsorption of the NO molecule. This is due to the fact that the environment of this oxygen atom experiences major reconstructions upon the adsorption of 0.5 ML NO (Fig. 5.3.1(a)). This oxygen is pulled out of the surface by 0.9 Å and forms an NO₂ molecule on the surface. So it is more sensible if one thinks of this oxygen as part of the NO₂ molecule rather than a part of the surface. We have calculated the binding energy of this NO₂ molecule to the rest of the surface (surface with 0.5 ML O vacancies) to be 0.5 eV per molecule; since this is much less than binding energy of NO to the (stoichiometric) surface (1.9 eV per molecule), upon heating the surface (for instance in a TPD experiment) NO₂ comes off the surface (rather than NO) leaving behind a surface with oxygen vacancies. This is in agreement with our previous findings that the most thermodynamically stable surface for the negatively poled surface is a surface with 0.5 ML oxygen vacancies [54].

Here we investigate the reason behind the attenuation of the NO magnetic moment upon adsorption from 1 to 0.5 $\mu_{\rm B}$ by investigating the binding of this NO₂ molecule formed on the surface. In Fig. 5.3.2(b) one can see the Highest Occupied Molecular Orbital (HOMO) and LUMO of NO₂ molecule. The shown orbital is the HOMO in spin up channel and LUMO in spin down, giving the NO₂ molecule a magnetic moment of 1 $\mu_{\rm B}$. This antibonding molecular orbital consists of O 2p states and



Figure 5.3.5: a) projected density of states (PDOS) on surface oxygen before NO adsorption. b) PDOS on a surface oxygen after NO adsorption without a NO molecule directly attached to it. c) PDOS on a surface oxygen after NO adsorption with a NO molecule directly attached to it.

also a hybrid of N 2p and 2s states. We have calculated E_F for the negatively poled surface with 0.5 ML oxygen vacancies and we have shown that it crosses the NO₂ LUMO. Based on this we predict that there will be an electron transfer to the NO₂ LUMO which is in channel down of spin. This is the reason for the quenched magnetic moment of the system. We also computed the charge transfer in real space, depicted in Fig. 5.3.6, which also confirms that electrons are being transferred to the NO₂ LUMO from the Pb atom nearby. Also Lowdin charges show an increase of 0.4 e on NO₂ molecule upon adsorption, which agrees well with attenuation of magnetic moment by 0.5 μ_B per molecule.



Figure 5.3.6: Electron transfer to the 0.5 ML NO_2 molecules which are formed after adsorption of 0.5 ML NO molecules on the negatively polarized stoichiometric PTO. Color red shows the regions with increased electron density and color blue shows electron depopulation.

5.3.2 O₂ molecular and dissociative binding

We find the ground state for O_2 intact and dissociative binding in each polarization. Binding energies seem to greatly depend on the polarization (Table 5.2). In positive polarization, the ground state of binding is dissociative, which is exothermic by 2.6 eV per molecule (in 0.5 ML coverage). We have tried several initial geometries for our relaxations, but the only metastable state that we find which resembles an intact binding mode is a stretched O_2 molecule (all other cases result in dissociated modes although we begin them from an intact binding mode) in which O atoms have an interatomic distance of 1.57 Å, compared to 1.24 Å for the gas phase O_2 molecule. This pseudo-intact mode has a very small magnetic moment of 0.3 $\mu_{\rm B}$ per molecule, and is 0.2 eV per molecule higher in energy than the ground state (dissociated O₂ molecules). As we will show in the next paragraph, this quenched magnetic moment is due to populating the O₂ antibonding states which are in spin down channel. The dissociative mode in positive polarization consists of separated O atoms located between Pb atoms as can be seen in Fig. 5.3.7(a). This structure has no magnetic moment.

In the paraelectric case, unlike positive polarization, the ground state is a weak intact binding (0.2 eV) mode. The dissociative binding mode in this case has almost the same geometry as in the positive case, but very different energetics (see Table 5.2) due to polarization-induced electronic reconstructions (changing polarization from paraelectric to positive changes the binding energy by the large value of 3.4 eV per molecule).

In negative polarization the intact binding ground state is a physisorbed molecule with negligible binding energy. The dissociative binding geometry is different from the positive and paraelectric case as can be seen in Fig. 5.3.7(b); now each oxygen adsorbate binds to a surface oxygen atom. This can be thought of as an oxygen atom forming a O_2 molecule with one of the surface oxygens after dissociation. The dissociative binding energy is very small in this case: 0.4 eV. Table 5.2 shows how changing the polarization of PTO can change the behavior of its surface toward oxygen. The positively polarized surface is very strongly interacting with O_2 , while negatively polarized and paraelectric polarizations are weakly interacting.

This is a very promising result, as one of the main challenges in the NO_x direct decomposition using conventional catalysis methods is that if the surface- NO_x interaction is strong enough to break NO_x molecules then it is very difficult to desorb oxygen atoms, which will gradually poison the catalyst [230] by blocking the catalytic sites. This problem is known as oxygen inhibition [232, 248, 249, 229, 231]. As was shown here we can avoid this problem by actively controlling surface-adsorbate interaction using ferroelectric polarization as a switch.

Table 5.2: Intact and dissociative binding energies for an O_2 molecule on the PTO surface as a function of polarization relative to O_2 in vacuum. More positive a number means the binding is more favorable. Negative number indicates a metastable state which is less favorable than O_2 in vacuum.

| Polarization | Intact Binding energy (eV) | ${ m Dissociative\ binding\ energy(eV)}$ |
|--------------|----------------------------|--|
| positive | 2.4 | 2.6 |
| paraelectric | 0.2 | -0.8 |
| negative | 0 | 0.4 |



Figure 5.3.7: The binding geometry for dissociated binding of O_2 to PTO surface on a) positively polarized surface, b) paraelectric and c) negatively polarized surface. Oxygen is shown in red, Pb (gray) and Ti is encaged in oxygen octahedra.

Figure 5.3.8 shows the level alignment of positively poled PTO with O₂ HOMO and LUMO. Here, the oxygen's LUMO lies 0.6 eV below E_F of the surface. Hence, there will be charge transfer to the O₂ LUMO. Since the O₂ LUMO is an antibonding state (π_{2p}^*), the O-O bond becomes loser and longer which (as is calculated in 0.5 ML coverage) is enough to make the molecule barrierlessly dissociate into O atoms. Figure 5.3.9 shows a metastable state which we referred to as "pseudo-intact mode"



Figure 5.3.8: Projected density of states (PDOS) on a Pb atom on the positive PTO surface and its relative alignment with O_2 HOMO and LUMO.

in previous paragraphs, in which the O₂ molecule is in between two Pb atoms and is stretched so that O atoms have an interatomic distance equal to 1.57 $\stackrel{\circ}{A}$ (as opposed to 1.24 $\stackrel{\circ}{A}$ in the molecule in gas). Here one can see that electrons are being transferred to the O₂ LUMO from Pb. This electron transfer to an antibonding molecular state in spin down channel justifies both the increase in the bond length of O₂ and also the quenching of magnetic moment from 2 $\mu_{\rm B}$ per molecule to almost 0.3 $\mu_{\rm B}$ per molecule.

The reason behind the difference in oxygen binding energies in different polarizations is the difference in position of conduction and valence band edges of the surface relative to the O_2 HOMO and LUMO. As Fig. 5.3.10 shows, unlike the positively polarized case, binding of the O_2 molecule to the paraelectric surface cannot be stable, since all the molecular and surface bands are either completely filled or completely empty, and also because of the relative positions of molecular states no charge transfer can happen between the molecule and the surface. Of course there are in principle two interactions that can lead to some stabilization of the O_2 -surface bond: 1) Interaction of the empty O_2 LUMO with the center of the filled surface O 2p band (which are 4.81 eV apart), 2) Interaction of the center of empty surface Pb 6p band with the O_2 HOMO (which are 4.55 eV apart). In both cases these are far separated in energy and have negligible interaction.



Figure 5.3.9: Real space electron transfer from Pb states to O_2 LUMO on positively poled Pb term. PTO. Color red shows gain of electron and blue shows loss of electron.

5.3.3 N_2 molecular binding

In all polarizations the surface interaction with N_2 molecules is found to be very small (0.1 eV for both positive and paraelectric polarizations, and 0.5 eV for negative). The dissociative binding modes are completely unstable, and the separated N atoms always recombine with each other (with no energy barrier) to form N_2 molecules which are weakly bound to the surface. The fact that N_2 in both intact and dissociative binding modes has negligible interaction with the PTO surfaces is good news for one who tries to achieve NO_x direct decomposition using PTO, as N_2 molecules can easily form (from separated N atoms which are the results of NO dissociation) and leave the surface.



Figure 5.3.10: Projected density of states (PDOS) on the surface Pb and O atom on paraelectric PTO surface and their relative alignment with O_2 HOMO and LUMO.

5.3.4 O and N atomic binding energies and their coverage dependence

Figure 5.3.11 shows the geometries of binding of O to PTO surface in different polarizations. One can see that on positively polarized PTO, oxygen bridges between two Pb atoms (top Pb atoms have experienced sliding as described before). On paraelectric surface oxygen binds to one of the surface oxygens in addition to two adjacent Pb atoms. Atomic binding energies for O on PTO as summarized in Table 5.3. Here we have calculated the binding energies relative to two different reference points: 1) O_2 molecule in vacuum, 2) O atom in vacuum. One can see that in positive polarization O favorably binds to the surface, while it does not bind to the paraelectric surface (we have detected a metastable state that is 0.7 eV per atom less favorable than O_2 in vacuum). On the negatively poled surface an atomic oxygen binding mode was not detected: we tried many different initial geometries for our relaxations, but all cases led to O_2 formation (the negatively poled surface is extremely oxidizing). The binding energy of this formed O_2 molecule to the rest of the surface (now with an oxygen vacancy) is -0.1 eV (unstable) relative to O_2 in vacuum, so it readily leaves the surface. This is in agreement with our findings in the previous chapter and our


Figure 5.3.11: Atomic binding of oxygen to a) positively poled b) paraelectric PTO surface (0.5 ML coverage). Oxygen is shown in red, Pb (gray) and Ti is encaged in oxygen octahedra.

Table 5.3: Binding energies (eV) for atomic adsorption mode of O atom on Pbterminated PTO as a function of polarization (0.5 ML coverage)

| | = | = , | |
|--------------|----------------------------|----------------------------|--|
| polarization | Binding energy relative to | Binding energy relative to | |
| 1 | O_2 in vacuum (eV) | O in vacuum (eV) | |
| positive | 3.0 | 6.3 | |
| paraelectric | -0.7 | 2.6 | |
| negative | NA | NA | |

prior work that the most thermodynamically stable surface for negative polarization has 0.5 ML O vacancies [54].

Now we look at the atomic binding of N to the PTO surface in different polarizations. The binding geometries are very similar to the case of oxygen atomic binding. Again, we have calculated the binding energies relative to two different reference points: 1) N₂ molecule in vacuum 2) N atom in vacuum. In negative polarization atomic binding of nitrogen to the surface is so unfavorable that we cannot detect even a metastable atomic binding mode: the N atom steals one of the surface oxygens and forms NO. Binding energy of this formed NO molecule to the surface (now with 0.5

| polarization | Binding energy relative to N_2 in vacuum (eV) | Binding energy relative to N in vacuum(eV) |
|--------------|---|---|
| positive | -1.6 | 3.3 |
| paraelectric | -3.6 | 1.3 |
| negative | NA | NA |

Table 5.4: Binding energies (eV) for atomic adsorption mode of N on Pb-terminated PTO as a function of polarization (0.5 ML coverage)

Table 5.5: Coverage dependences for N and O atomic binding energies (relative to energy of the atom in vacuum) for positively polarized PTO surface.

| 0. | , | |
|-----------|-------------------------|-------------------------|
| Course mo | N Binding energy (eV) | O Binding energy (eV) |
| Coverage | relative to N in vacuum | relative to O in vacuum |
| 0.25 ML | 4.3 | 6.1 |
| 0.5 ML | 3.3 | 6.3 |
| 1 ML | 2.3 | 4.6 |

ML oxygen vacancies) is 0.3 eV (weakly bound) relative to NO in vacuum, so it easily leaves the surface. As it can be seen in Table 5.4, polarization affects the binding energy of N to the surface by more than 2 eV per atom.

We have calculated the coverage dependences for both N and O atomic bindings to the positively poled surface. The results are summarized in Table 5.5 in which one can notice two different trends. For N, changing the coverage from 0.25 ML to 1 ML decreases the binding energy per atom by 1 eV every time we double the coverage, in a linear fashion. But for O, first going from 0.25 ML coverage to 0.5 ML increases the binding energy by 0.2 eV per atom. Then increasing the coverage further to 1 ML decreases the binding energy by 1.7 eV.

Our first attempt to rationalize and understand these trends was to count extra electrons per adsorbate on the surface for each coverage. Oxygen and nitrogen are both very electronegative atoms [250, 251]: they can accordingly accommodate 2 and 3 electrons respectively and become closed shell. At 0.25 ML coverage in positive polarization, we have almost 4 extra electrons per adsorbate. This many electrons can stabilize either N or O, thus we expect large binding energies for both species at this coverage. In 0.5 ML coverage we have almost 2 extra electrons per adsorbate. This is still enough to completely stabilize oxygen and make it closed shell but it is not enough to completely stabilize nitrogen. This is why binding energy per atom almost remains the same for O binding but it decreases significantly for N binding. In 1 ML coverage we have almost 1 extra electron per adsorbate so even oxygen cannot reach closed shell configuration. That is why going from 0.5 to 1 ML coverage, the oxygen binding energy per atom drops significantly. This reasoning is based on the electron transfer picture from the surface to the electronegative adsorbate. In the case of transition metal surfaces there are several studies to support this picture, which shows itself as an induced dipole moment on the surface and an increase in the work function [252, 253]. The induced dipole moment is shown to decrease with the coverage showing less electron transfer to the adsorbate as a result of the adsorbate-adsorbate repulsion mediated by the surface states [254, 255, 256]. In the next paragraphs this simple electron transfer picture will be confirmed based on the surface and adsorbates' electronic structure.

The problem of coverage dependence (self-poisoning) of nitrogen, oxygen, sulfur and carbon adsorbate are discussed in the literature, but mostly on transition metal surfaces and not on perovskite or ferroelectric surfaces. In a work published in 2009 by Kitchin [257], the coverage dependence of oxygen, nitrogen, and carbon atomic binding energies to the Pd (111) surface is addressed based on a simple d-band model [258, 259, 260, 17]. Kitchin mentions a coverage dependence for N and O atomic binding energies spanning about 1.5 eV range from low coverage (0.2 ML) to full coverage (1 ML). He also showed that the dependence of adsorption energies on coverage varies systematically from C to O and in a linear fashion for each, carbon being the most sensitive and oxygen the least. Here in our work we see a coverage dependence for adsorption energies that spans even a more significant range of 2 eV. Unlike nitrogen atoms on PTO, and unlike the general trends seen in literature for



Figure 5.3.12: Electron density transfer in real space upon adsorption of 0.25 ML nitrogen to the positively poled PTO surface. N atoms bridge in between Pb atoms. Color red indicates the region of space which electrons migrate to, while the blue indicates the region which electrons migrate from upon adsorption of 0.25 ML nitrogen atoms.

adsorbates like S, C, O and N on various transition metal surfaces [261, 257, 262, 263, 256, 255, 254, 264, 265, 266], the coverage dependence for oxygen is not linear in the 0.25 to 1 ML range. In the previous paragraph we rationalized this non-linear relation for O adsorption on positively-poled PTO surface.

Figure 5.3.12 shows the electron density transfer in real space upon adsorption of 0.25 ML nitrogen to the positively poled PTO surface. This shows the electrons leave the lead atoms and migrate to the nitrogen unoccupied atomic states (2p). The spherical symmetry of the charge transferred to N atom indicates that N has reached a closed shell configuration by accepting 3 electrons from the surface Pb atoms.

Figure 5.3.13 confirms our electron transfer picture (from the surface to the adsorbate). As one can notice in this figure, in low coverage (0.25 ML) the adsorbates' 2p states remain very sharp (almost atomic-like). N 2p states are closer to the Fermi energy of the surface (higher in energy) than O 2p states. This is simply saying that oxygen is more electronegative than nitrogen.

Figure 5.3.13 shows the sharp atomic-like O 2p states are below E_F in both 0.25 and 0.5 ML coverage, which means oxygen reaches a closed shell configuration in both. It can be seen both from the sharp nature of the O 2p state and also its small hybridization with the surface Pb 6p states that the nature of O binding to the surface is primarily due to electron transfer and not covalency. In 1 ML coverage, the O 2p state is no longer fully occupied and it experiences more dispersion due to oxygen-oxygen interactions.



Figure 5.3.13: Projected density of states (PDOS) for the surface Pb atom (which dominates the surface conduction band) and surface oxygen (which dominates the surface valence band), along with density of states of adsorbed oxygen and nitrogen for 3 different coverages.

As Fig. 5.3.13 shows in 0.25 ML coverage, the sharp atomic-like N 2p states are below the Fermi energy. It can be seen in 0.25 ML coverage that there is more hybridization between Pb 6p and N 2p states relative to oxygen in the same coverage. This is due to the fact that N 2p states are higher in energy and they are closer to both the Fermi energy and the center of the Pb 6p band. As was discussed above, in 0.5 ML N coverage the surface doesn't have enough electrons to fully populate the empty N 2p states: this is confirmed in Fig. 5.3.13 in which some of the N 2p states in 0.5 ML coverage (that were below E_F in 0.25 ML coverage) are now depopulated and are above the Fermi level. This is also the case in 1 ML N coverage. One should note that due to a larger hybridization between N 2p and Pb 6p states relative to the case of oxygen, there is a stronger surface band mediated interaction among the nitrogen adsorbates relative to oxygen atoms. This can be best seen in 0.5 ML coverage, in which we still have sharp atomic-like oxygen states while the N 2p band has a noticeable dispersion due to surface-band-mediated interaction with other nitrogen adsorbates.

5.3.5 NO dissociated binding

Now that we have investigated N and O atomic binding to the PTO surface, we turn our attention to NO dissociated binding. As can be seen in Table 5.6, in 0.25 ML NO coverage (as opposed to 0.5 ML coverage), the dissociated binding mode is more favorable than intact molecular binding.

Table 5.6: Binding energies (in eV and relative to NO in vacuum) for the NO molecule in both dissociated and intact binding mode for two different NO coverages. In 0.5 ML coverage, intact mode is more favorable, while in 0.25 ML the opposite is true.

| Binding mode | $0.25 \mathrm{ML}$ | $0.5 \mathrm{ML}$ |
|--------------|--------------------|-------------------|
| Dissociated | 2.4 | -0.4 |
| Intact | 1.9 | 1.5 |

This coverage dependence can be understood based on the charge transfer picture explained in the previous section. In 0.5 ML NO coverage the surface has only 2 extra electrons per 2 adsorbates (1 N and 1 O). This number of electrons can make the more electronegative O reach closed-shell configuration, but then there is no electron left to stabilize N binding to the surface. This justifies why in this coverage NO dissociated binding is not stable (as confirmed in Table 5.6). In 0.25 ML NO coverage there are 4 electrons per 2 adsorbates (1 N and 1 O), this number of extra electrons can make the more electronegative O reach closed shell configuration, while 2 electrons are left for N which help stabilize its binding to the surface. Based on this reasoning we predict that the dissociated binding energy will maximize at 0.2 ML NO coverage and stays almost constant for smaller coverages.

The large dissociative binding energy for the NO molecule in low coverages (≤ 0.25 ML), and the fact that dissociation is the ground state of binding (as opposed to intact binding), means one can dissociate NO molecules using the positively polarized PTO surface in low coverages (≤ 0.25 ML). We have calculated the NO dissociation barrier, using the constrained relaxation method, to be 0.7 eV. Based on our calculations, in 0.25 ML NO coverage, it is more favorable for separated N atoms to form N₂ molecules (N diffusion barrier on positively poled PTO is calculated to be ≈ 1 eV which is a reasonably small value and lower than O diffusion barrier by 0.1 eV) and leave the surface behind with 0.25 ML O adatoms (by 2.7 eV per N₂ molecule).



Figure 5.3.14: Comparison of transition state and dissociated binding mode for NO on positively poled PTO (0.25 ML coverage). Side view of the supercell is shown on top, while a top view is shown at the bottom. The color code is N (pale blue), O (red), Pb (gray), and Ti are encaged in blue oxygen octahedra. At transition state the N-O distance is ≈ 1.89 Å while at the dissociated state it is ≈ 3.86 Å. The Pb-O distance is 2.26 and 2.06 and Å in the TS and dissociated state, respectively. The Pb-N distance is 2.18 and 2.06 Å in the TS and dissociated state, respectively.



Figure 5.3.15: Comparison of the transition state and the dissociated binding mode for NO on Pt (001). Side view of the supercell is shown on top, while a top view is shown at the bottom. The color code is N (pale blue), O (red), Pb (gray), and Ti are encaged in blue oxygen octahedra. At transition state the N-O distance is ≈ 1.95 Å while at the dissociated state it is ≈ 3.55 Å. The Pt-O distance is 2.04 and 2.08 and Å in the TS and dissociated state, respectively. The Pt-N distance is 1.93 and 1.96 Å in the TS and dissociated state, respectively.

Thus one can dissociate NO and form N₂ in low adsorbate coverages (≤ 0.25 ML), but once the surface begins to be saturated with oxygen atoms (either from NO dissociation or O₂ dissociation), NO decomposition can no longer happen. Then one can switch the polarization to the negative in which the oxygen binding to the surface is very weak and one can clean off the oxygens from the surface, bringing back the



surface to the pristine state and ready for the next polarization cycle.

Figure 5.3.16: Comparison of the electronic structure of the transition state (TS), dissociated and intact binding state for NO on the transition metal surface Pt (001). In panel a) projected density of states (PDOS) on adsorbed nitrogen, in panel b) PDOS on adsorbed oxygen. The electronic structure of the transition state resembles the electronic structure of the dissociated state rather than intact binding.

Figure 5.3.14 depicts the transition state for NO dissociation on positively poled PTO (0.25 ML coverage) found using the constrained relaxation method. The N-O distance is ≈ 1.9 Å and looks like a highly stretched molecule. This is similar to the case of dissociation of diatomic molecules on transition metal surfaces (see Fig. 5.3.15), and similarly one of the atoms is already close to its final site, while the other is on its way to its final site [41, 267, 268]. In the case of transition metals [41], for the "stretched" transition states, the electronic structure of the transition state (TS) is much more like that of the adsorbed atoms than that of the adsorbed

molecule, as also confirmed by our calculations (see Fig. 5.3.16). However, in the case of NO dissociation on ferroelectric $PbTiO_3$, as can be seen in Fig. 5.3.17, we do not see such a resemblance in the density of states. In the case of transition metals, as exemplified by NO binding to Pt (001) (Fig. 5.3.16), there is a significant hybridization between the adsorbate and metal surface states (d states), in both the TS and dissociated state. In contrast, on positively polarized PTO there is not a significant hybridization between the adsorbate and surface states in dissociated state (as opposed to the TS). We believe this is correlated to the fact that, in the case of positively polarized PTO, unlike transition metal surfaces, the system has a considerable band gap ($\approx 2 \text{ eV}$ in our DFT calculations) and the adsorbate states either align with the edge of the valence band (oxygen) or the middle of the band gap (nitrogen), as can be seen in Fig. 5.3.13. Thus, in order to create a significant covalent bond between the adsorbate and the surface states, the surface should mechanically deform to make surface states available close to adsorbate states; that requires an energy cost to create the deformation. In the case of the positively poled surface there is a reservoir of high energy doped electrons in the edge of the conduction band, which can transfer to the low-energy atomic-like adsorbate states and stabilize their binding with the surface (see Fig. 5.3.18), with no need to pay an energy cost associated with the mechanical surface deformations. The simultaneous existence of a parallel channel for binding (charge transfer), in addition to covalent surfaceadsorbate interactions, and an energy gap close to the Fermi energy, is thought to be the reason that unlike transition metal surfaces there is not a significant hybridization between the surface and adsorbate states, in the dissociated binding case. This is an interesting observation that can potentially open an avenue for future research focusing on breaking the scaling relations between the TS and dissociated binding energies, which has been identified as a limiting factor in designing efficient and selective catalysts [1, 3, 131]. The existence of extra doped charges on the surface of



Figure 5.3.17: Comparison of the electronic structure of the transition state (TS), dissociated and intact binding state for NO on positively poled $PbTiO_3$ (001). In panel a) projected density of states (PDOS) on adsorbed nitrogen, in panel b) PDOS on adsorbed oxygen. Unlike the case of dissociation on transition metals, the electronic structure of the transition state does not resemble the electronic structure of the dissociated state.

a gapped oxide system might play the role of the extra degree of freedom, sought in the transition metal literature, that has been deemed necessary to break away from the scaling relations.

5.3.6 NO₂ intact and dissociative binding

As was shown in the previous section using the scheme we propose, NO can be dissociated into N₂ and O₂ in low coverages (≤ 0.25 ML). Here we show that one can use the positive polarization to decompose NO₂ into NO (which can later be dissociated into



Figure 5.3.18: Comparison of NO binding to positively poled PbTiO₃, in transition and dissociated state using real space electron redistribution. Nitrogen is shown in pale blue, O (red), Pb (gray) and Ti is encaged in oxygen octahedra. Top panels show the side view, while the bottom panels show the top view of the surface. The color red shows the regions of space which electrons migrate to, while the blue regions indicate electron depopulation. As it can be seen, in the dissociated state, as opposed to the TS, there is not a significant hybridization between the adsorbate and surface states, and the charge transfer is between the surface to the spherically symmetric atomic like adsorbate states. An RGB scale has been used for 2-d electron redistribution sections in which red shows positive (population by electrons), blue indicate negative (depopulation by electrons) and green is neutral.

| Polarization | Binding energy (eV) | Binding Geometry |
|---------------------------|------------------------|---|
| Positive (intact) | 1.9 | ${ m NO}_2$ bridges between two leads |
| Positive (dissociated) | 2.3 | O bridges between two Pb; NO physisorbed |
| Paraelectric (intact) | 0.5 | Physisorption |
| Negative (dissociated) | 1.5 | forms Nitrate with surface O atom |

Table 5.7: NO_2 binding energies and binding geometries on Pb terminated PTO as a function of polarization and binding mode.

N and O in the same polarization) and O even in higher coverages (0.5 ML). Table 5.7 summarizes the binding energies and binding geometries for different polarizations. NO₂ interacts strongly with positively poled PTO surface. Figure 5.3.19 depicts the intact binding of NO₂ to the positively poled PTO surface. The mechanism behind this binding is a significant electron transfer from the Pb conduction band to the NO₂ antibonding LUMO, which results in weakening and elongating the N-O bond (by 0.13 Å relative to NO₂ in vacuum), thus aiding NO₂ dissociation on this surface. The NO₂ dissociation barrier calculated using the constrained relaxation method is found to be negligible. One notes that in positive polarization the ground state of binding for NO₂ is dissociative rather than intact.



Figure 5.3.19: Electron transfer from the Pb conduction band to the NO₂ LUMO on the positively poled PTO surface (0.5 ML coverage). N is shown in pale blue, O (red), Pb (gray) and Ti (Cyan). A side view is shown on the left, and a top view is depicted on the right hand side. Regions of space which electrons migrate to are indicated by color red, while the blue indicates the region which electrons migrate from upon adsorption of 0.5 ML NO₂.

5.3.7 SO₂, H_2O and CO_2 binding

Sulfur containing compounds including SO_2 molecules are among the pollutants that can be produced during fuel combustion. In addition to being poisonous for the environment and the human body (causing acid rain and respiratory system problems), they can also significantly poison the catalytic properties of the catalyst (because of high reactivity with the surface [269, 270]) and if not effectively removed can eventually render it inactive. Thus it is desirable to have a scheme that leads to removal of these molecules from air or the catalyst surface.

What follows shows that, potentially, one can use ferroelectric $PbTiO_3$ to strongly adsorb this molecule in positive polarization, and then release it by going to the paraelectric phase (for example by going beyond the Curie temperature) or the negatively poled phase (in form of SO_3). Table 5.8 summarizes the binding energy of SO_2 molecule to PTO. Fig. 5.3.20 shows the binding geometries for SO_2 in different polarizations. In positive polarization SO_2 interacts with the surface strongly. SO_2 is situated above the surface such that it bridges between the two adjacent lead atoms that form a dimer (a banana bond forms between them). Here the S atom is closer to the middle of the two Pb while the two oxygen atoms are close to each Pb. In the paraelectric case the binding energy is much smaller relative to positive polarization, and also the binding geometry is different; now SO_2 binds to a surface oxygen from the S site. In negative polarization SO_3 forms on the surface as SO_2 takes one of the surface oxygens away, so one should be careful in interpreting the binding energy of SO_2 to this surface. In negative polarization it is more informative if we talk about binding energy of SO_3 to a surface with 0.5 ML oxygen vacancy which we calculated to be very close to zero. So exposure of the negatively poled stoichiometric PTO to SO_2 molecules causes SO_3 gas formation, and brings the stoichiometric surface to its most stable thermodynamical state, which is a surface with 0.5 ML oxygen vacancies [54]. As we have seen before, a similar situation happens after exposure of the negatively poled surface to NO molecules, N or O atoms: they all reduce the stoichiometric surface to its thermodynamical ground state which has 0.5 ML O vacancy. All these findings underline the highly reducing property of the positively poled surface and the strongly oxidizing property of the negatively poled surface.



Figure 5.3.20: Binding geometries for SO_2 on the Pb terminated PbTiO₃ surface in different polarizations (0.5 ML coverage): a) positively polarized, b) paraelectric, and c) negatively polarized surface. S atoms are shown in yellow, O (red), Pb (gray) and Ti are shown encaged in oxygen octahedra. On the negatively poled surface, 0.5 ML SO_2 steals 0.5 ML oxygen from the surface octahedra and forms 0.5 ML SO_3 hovering over the surface.

Table 5.8: Binding energies of SO₂, H₂O and CO₂ (in eV) on stoichiometric Pb terminated PTO as a function of polarization (0.5 Ml coverage). Binding energy of SO₂ to negatively poled surface (marked by *) should be interpreted with caution, in this case SO₂ binds to the surface Oxygen and forms SO₃ which is weakly bound to the rest of surface (with 0.5 ML O vacancy)

| Polarization | SO_2 | H_2O | $\rm CO_2$ |
|--------------|--------|--------|------------|
| positive | 1.8 | 0.3 | 0.1 |
| paraelectric | 0.7 | 0.4 | 0.1 |
| negative | 1.2* | 0.8 | 0.1 |

One can use stoichiometric negatively polarized PTO to produce SO_3 molecules. The current method of producing sulfuric acid is the contact process which was patented in 1831 by Peregrine Phillips [271, 272]. At the heart of this process is the rate limiting oxidation of SO_2 to SO_3 in the presence of catalysts like Pt or V_2O_5 . But as was shown above, negatively poled PbTiO₃ has a strong interaction with SO_2 molecules (1.2 eV per molecule adsorption energy) and upon adsorption SO_3 is formed with no barrier and has a negligible binding energy to the surface. So the negatively poled PTO surface may be an ideal catalyst for oxidation of sulfur dioxide to sulfur trioxide. After the release of SO_3 we are left with the most thermodynamically stable surface, which is a surface with 0.5 ML oxygen vacancies [54]. But one can flip the polarization to positive or paraelectric which leads to adsorption of oxygen and replenishment of the vacancies with oxygen atoms. We can do this cyclically and convert SO_2 molecules into SO_3 .

One should note that although in positive polarization we have a strong interaction between the surface and SO₂ molecule, in the scheme that we propose, which uses a cycle of negative and positive polarizations as NO_x direct decomposition catalyst, there is no important poisoning by SO₂ molecules, as in the negative polarization SO₂ molecules leave the surface in form of SO₃ molecules.

Using DFT, we have examined SO₂ molecular properties. The S-O distance is calculated to be 1.46 Å and the $\angle OSO$ angle is calculated to be 119°: both are in excellent agreement with the literature values of SO distance and $\angle OSO$ of 1.43 Å and 119° [273, 274]. Figure 5.3.2 shows the HOMO and LUMO of the SO₂ molecule which are almost 3.5 eV apart in energy in our GGA-DFT calculations. The HOMO consists of 2×37.5% O 2p, 16.0% S 3s and 9.0% S 3p orbitals. The LUMO consists of 2×24% O 2p and 52% S 3p orbitals.



Figure 5.3.21: Level alignment of SO_2 molecule's HOMO and LUMO with conduction and valence bands of the positively polarized PTO surface. This level alignment predicts that the bonding between SO_2 and the positively poled surface has charge transfer nature to SO_2 LUMO. The level alignment between the left and right hand side has been achieved by aligning the semi core states in the bulk region of each supercell.

On the left side of Fig. 5.3.21 one can see the level alignment of the SO₂ molecule's HOMO and LUMO with conduction and valence bands of positively polarized PTO. One notices that the SO₂ LUMO is below the Fermi energy of the surface. So one predicts that there will be electron transfer to the SO₂ LUMO and this is the mechanism behind the strong binding of the molecule to positively poled surface. This is confirmed by a) looking at the real space charge density transfer (Fig. 5.3.22) and b) looking at the projected density of states on the surface atoms and SO₂ molecule after its adsorption to the surface shown on the right side of Fig. 5.3.21. In this figure one notices that, as predicted by looking at the alignment of SO₂ molecule and clean positively poled surface, what used to be the SO₂ LUMO is now filled beneath the Fermi energy, and one can see that this state is slightly shifted down in energy as a

result of interaction with Pb 6p states. One also notices that the Pb 6p states that used to host extra electrons on the positively polarized surface now are above the Fermi level and have transferred their electrons to the SO₂ LUMO. Furthermore, the SO₂ HOMO is slightly pushed up in energy as a result of interaction with the PTO valence band, and has pushed the valence band slightly lower in energy. It should be noted that the SO₂ states that are seen on the right side of Fig. 5.3.21 above the Fermi level are mostly states whose energy is higher than the SO₂ LUMO in a energy range that coincides with that of Pb-p states above Fermi level. It is also noteworthy to compare the Lowdin charges on SO₂ after and before adsorption to the surface. Our calculations shows an increase of Lowdin charges by 0.85 e, which agrees with the charge transfer picture. This is associated with an increase in the S-O bond length by 0.15 Å relative to SO₂ in gas form. This is a result of the fact that SO₂ LUMO is an antibonding state as can be seen in Fig. 5.3.2.



Figure 5.3.22: Charge transfer in real space after SO_2 adsorption on the positively poled PbTiO₃ surface (red showing increase and blue showing a decrease in electron density). One can see the charge transfer to the SO_2 LUMO from Pb 6p states, which is the main mechanism of binding for strong SO_2 adsorption to positively poled PTO.

One remarkable feature of the SO₂ density of states after adsorption, as seen in Fig. 5.3.21, is the sharp SO₂ LUMO band. This hints that there is a small covalency between the SO₂ molecule and the surface, and the stabilization of the binding is mostly due to the charge transfer (to the SO₂ LUMO from surface Pb). But why is there such a small covalency between the SO₂ LUMO and Pb 6p band? The answer can be found in Fig. 5.3.23. The edge of the surface conduction band as is also shown in Fig. 4.3.11 consists of a hybrid of Pb 6p_x and Pb 6p_z orbitals. This leads to (+) sign in between dimers above the surface, and (-) sign outside the dimers below the surface (Fig. 5.3.23). Because of the special symmetry of the SO₂ LUMO (and because it consists of 52% S 3p and 48% O 2p states), its total overlap with this banana bond is almost zero. This is the reason behind the very weak hybridization of the SO₂ LUMO and the surface Pb 6p band.



Figure 5.3.23: Sign of the wave function for the SO_2 LUMO and the edge of the surface conduction band (Pb 6p). There is total overlap of almost zero between the SO_2 LUMO and the surface banana bond which is located in between two dimerized surface Pb atoms.

Table 5.8 summarizes the binding energy of H_2O and CO_2 molecules to the PbTiO₃ surface as a function of polarization (in 0.5 ML coverage). In the case of H_2O the binding energies are small in both positive and paraelectric cases. On the negatively poled surface, the binding energy is larger but this does not create an H_2O poisoning problem for a cyclic scheme in which the polarization is cyclically switched: one can

desorb H_2O in positive and/or paraelectric polarizations.

It can also be seen in Table 5.8 that the CO_2 interaction with the surface is small regardless of polarization: there will be no poisoning effect caused by it. It is interesting that the CO_2 binding energy to the surface doesn't show any polarization dependence unlike all the molecules discussed up to this point. The reason for this special behavior can be seen in Fig. 5.3.24 which depicts the level alignment of the CO_2 HOMO and LUMO with conduction and valence bands of the ferroelectric PTO surface. CO_2 has a low energy stable HOMO and a large band gap (8.36 eV) in our GGA calculations, and the middle of the CO_2 band gap almost coincides with the middle of the paraelectric PTO band gap. What this means is that the CO_2 HOMO and LUMO in all 3 polarizations are far apart in energy from both the Fermi energy and the band edges of the surface partially filled bands (see Fig. 5.3.24). This translates into weak binding regardless of the polarization.



Figure 5.3.24: Alignment of the CO_2 HOMO and LUMO with PbTiO₃ valence and conduction band for different polarizations.

5.3.8 Positively-poled PTO as a CO oxidation catalyst or a TWC

As described above, positively-poled PbTiO₃ prefers to be covered with 0.5 ML O adatoms (that can be provided barrierlessly by O₂ dissociation from the gas), which help accommodate extra doped electrons. We numerically investigate the interaction of this oxygen rich surface with 0.5 ML CO molecules, and we find that it is energetically favorable for the system by ≈ 0.35 eV per adsorbate molecule to have 0.5 ML CO₂ weakly adsorbed (0.1 eV binding energy as mentioned above) on the surface rather than having 0.5 ML CO physisorbed on the surface with 0.5 ML O adatoms. Thus the positively poled oxygen rich PTO surface can be used to oxidize CO into CO₂. The formation energy barrier has been calculated using the constrained relaxation method to be ≈ 0.2 eV. Thus positively poled PTO once exposed to a mixed intake of O₂ and CO (assuming the surface is kinetically trapped to be Pb rich and does not gradually develop 0.5 ML Pb vacancies, which is the most thermodynamically stable state) might act as an effective CO oxidation catalyst.

Taking off the surface extra oxygens using CO oxidation can create the low coverage environment necessary for NO dissociation and thus catalyzing the $NO_x \rightarrow N_2 + O_2$ reaction. Although this does not fall into the category of direct NO_x decomposition, it can potentially be an alternative to the precious metals (like Pt or Rh) which are currently being utilized in three way catalysts (TWC) in which a mixed intake of CO and NO is converted to CO_2 , N_2 and O_2 .

5.4 NO on non-stoichiometric Pb terminated PbTiO₃

As was mentioned before, in this chapter we were focused on the chemistry of stoichiometric Pb terminated PTO surfaces. The reason is we are most interested in the behavior of a sample that is cyclically switched between opposite polarizations. Nevertheless, we also study the surface chemistry of the steady state PTO surfaces which, in addition to geometric and electronic reconstructions, have experienced nonstoichiometric atomic reconstructions. Table 5.9 summarizes the binding energy of NO to such surfaces. If we compare these numbers to Table 5.1 we can see that the same trend versus polarization holds although the magnitude of the effect has attenuated. In negative polarization (with 0.5 ML O vacancies) NO attaches to the surface oxygen, which can be thought of as an NO_2 molecule attached to the rest of the surface (surface with 1 ML O vacancy). In the case of 0.5 ML of NO on stoichiometric negatively poled PTO, it was noted that 0.5 ML NO_2 molecules form, which are weakly bound to the surface (0.5 eV per molecule) and they can be desorbed from the surface upon heating (leaving the surface with steady state configuration, i.e., 0.5 ML O vacancy). Here in the case of thermodynamically stable negatively poled PTO, the surface already has 0.5 ML O vacancies, so one predicts that this NO_2 is much more strongly bound to the rest of the surface (i.e., surface with 1 ML O vacancy). Our calculations confirms this, as the NO_2 binding energy to the rest of the surface (surface with 1 ML O vacancies) is 2.6 eV.

The main observation here is that the thermodynamically stable surface states (steady states) of ferroelectrics do not offer a particularly interesting surface chemistry. The reason behind this is the fact that the novel surface chemistry observed on electronically reconstructed (stoichiometric) ferroelectric surfaces was a result of the polarization doped electrons/holes on the surface. As was mentioned before, on thermodynamically stable ferroelectric surfaces, atomic reconstructions provide these doped carriers with energetically favorable states, thus making it harder (if not impossible) for the doped charges to interact with adsorbates. Thus, we believe the avenue that can unveil the novelty of ferroelectric based chemistry and catalysis is to periodically perturb the system away from its equilibrium (steady state) by the use of external fields (pressure, temperature, electric, magnetic, etc.) and exploit the

tendency of ferroelectrics to go back to their thermodynamically stable ground state

to drive forward desirable reactions.

Table 5.9: NO binding energy to thermodynamically most stable (steady state) PTO structures at each polarization. One should note that positive polarization has two different stable phases; also one should note that the steady state for the paraelectric case is the stoichiometric surface.

| Steady state surface | Binding energy (eV) | Binding geometry |
|-------------------------------------|------------------------|---|
| positively poled 0.5 ML O adatom | 0.5 | physisorption |
| positively poled 0.5 ML Pb vac. | 0.5 | physisorption |
| paraelectric stoichiometric | 0.3 | physisorption |
| negatively poled 0.5 ML O vac. | 1.0 | forming NO ₂ with surface O |

5.5 Conclusions

We studied the electronic structure of the Pb terminated PbTiO₃ (PTO) surface as a function of polarization. We investigated various surface reconstructions in each polarization and the mechanisms behind each of them. We described the polarization dependent surface chemistry of NO, NO₂, N₂, and O₂ molecules in both dissociated and intact binding modes on this surface, and we studied some of the coverage dependences. We discovered that polarization can be used as a switch to control the binding energies of most of these species, and showed that using a cycle of positive and negative polarizations we can overcome the oxygen inhibition problem which has been a critical problem for developing a NO_x direct decomposition catalyst (which is an open challenge in automotive emission control industry). The only limitation in this scheme using the bare PTO surface is that NO decomposition only happens in low coverages. This is why in order to increase the efficiency of this method we investigated the systems in which the PTO surface is terminated with a monolaver of active transition metal oxide (as continuation of perovskite structure), which seems very promising even in higher coverages. This is described in the next chapter.

An important observation that was made here, that can be further explored in more detail in future work, is the breaking of symmetry between the electronic structure of the transition and dissociated states on positively polarized PbTiO₃, which we trace back to the existence of an energy gap close to the Fermi energy and of a high energy (polarization doped) electron reservoir that creates a parallel mechanism for binding (in addition to covalent binding with the surface, as per transition metal surfaces) that can potentially act as the extra degree of freedom that is deemed necessary and desirable to break away from the scaling relations (observed on transition metal surfaces) that impose fundamental limitations on the surface catalytic properties.

Chapter 6

Catalysis via oxide monolayers on ferroelectrics

6.1 Introduction

In agreement with the Sabatier principle, the plot of catalytic activity versus molecular adsorption strength for a variety of catalytic surfaces shows a maximum at an intermediate binding strength: a "volcano plot" [27, 275, 276]. Sensibly, much effort in catalyst design aims to find surfaces whose binding energetics are "just right" for the molecules involved in key steps of a reaction [2, 42, 277, 278, 279].

A priori, it would be desirable to have a single surface whose activity is tunable, via external control of an order parameter, from strong binding and rapid dissociation to weak binding and easy desorption. One possibility is the surface electron density: e.g., the surface chemistry of SnO₂ nanowires [280, 281] or graphene [282] is controllable using a gate voltage which alters the electron density. An alternative is a ferroelectric surface: when the ferroelectric has an out of plane polarization (i.e., electrical dipole density) \vec{P} , there is a surface charge density $\vec{P} \cdot \hat{n}$ which must be compensated by changes of surface charge density. Switching the direction of the polarization changes the surface's electronic states [283, 194, 58] and can promote specific reactions. Previous work has highlighted the potential benefit of depositing a monolayer of a transition metal oxide on a ferroelectric surface for enhancing surface reactivity [54]. As we describe below, these active monolayers can overcome the thermodynamic stability problems that have hindered prior applications of similar ideas: for example, transition metal layers, while chemically active in theory, do not wet ferroelectric surfaces but instead aggregate to form bulk-like nanoparticles [284, 285, 286, 287]. We show that the oxide monolayers we propose, when used in a mode where the polarization is flipped cyclically, lead to enhanced catalytic behavior that is not limited to an intermediate range of adsorbate-substrate interaction strength (i.e., the Sabatier principle) but instead takes advantage of both sides of the volcano. This approach is general and can be applied to a variety of reactions. We demonstrate its utility for simultaneous direct decomposition of NO_x (i.e., NO and NO_2) into N_2 and O_2 [288, 44, 228, 289, 290, 51, 291, 292, 293] and CO oxidation into CO_2 . Both reactions are critical in the automotive emission control industry [289, 290, 51, 291, 294].

Here, we quantitatively show how one can use the ferroelectric polarization in a cyclic manner while simultaneously exploiting the thermodynamical driving force for reconstructions of the ferroelectric surfaces [204, 54, 295, 296, 206] to efficiently drive desired reactions and create a complete catalytic cycle. This new approach can bring us beyond the limits of the Sabatier principle. We describe a class of systems that could be optimized to perform a wide range of reactions and that, unlike transition metal thin films on ferroelectrics [284, 287, 285], are thermodynamically stable and thus, in principle, can be fabricated experimentally.

6.2 NO_x direct decomposition via RuO_2 monolayer on PTO

The fact that bulk RuO_2 catalyzes NO decomposition [297, 298] motivates us to place a RuO_2 monolayer on the (001) PbO-terminated PbTiO₃ (PTO) surface which is its thermodynamically stable termination [54, 299, 214]. Table 6.1 displays first principles calculated results for the polarization-dependent binding energies for a number of molecules on RuO₂-terminated PTO. In this work, more positive binding energies indicate more energetically stable configurations. Positive polarization (along the surface normal vector) leads to extra electrons appearing on the surface to compensate the surface charge density $(\vec{P} \cdot \hat{n})$: this creates the strong interaction regime sporting large binding energies. Negative polarization adds extra holes to the surface and pushes the surface to the weak-binding, desorptive regime in almost all cases. Encouraged by this, we calculate the NO dissociation, N_2 formation and O_2 dissociation barriers in positive polarization and present them in Table 6.2. The tables show that for positive polarization (i) O_2 molecules readily dissociate into bound O atoms, (ii) a fraction of the NO molecules will dissociate into bound N and O atoms, and (iii) the small N_2 formation barrier means that resulting N atoms readily form N_2 (instead of reforming NO) which is weakly bound and leaves the surface. Up to this point, some NO molecules have dissociated but the surface has become saturated by strongly bound O atoms (i.e., oxygen inhibition), a standard problem in NO direct decomposition catalysis [229, 230, 248, 232, 231, 249]. Switching the polarization at this point strongly destabilizes the bound atomic O: the O atoms form O_2 which is bound weakly and desorbs easily. This returns us to a pristine surface that is ready for the next polarization cycle.

We envision operating the system in a cyclical manner by repeatedly switching polarization between a reducing surface (P > 0) and an oxidizing surface (P < 0)

Table 6.1: Polarization-dependent binding energies in eV for intact and dissociated molecules involved in NO_x direct decomposition on RuO_2 -PbTiO₃ and CrO_2 -PbTiO₃ for positive, paraelectric and negative polarizations, indicated by (+), (0), and (-), respectively for 0.5 monolayer (ML) coverage. More positive numbers denote increased stability. Binding energies are relative to the energy of the gas phase molecules. NS means no mechanically stable configuration exists. Negative values indicate mechanically stable metastable states (local minima) that are less stable than the gas phase molecules.

| Binding | Modo | RuO ₂ -PTO | | CrO ₂ -PTO | | | |
|----------------|--------|-----------------------|-----|-----------------------|-----|-----|------|
| Molecule | Mode | + | 0 | - | + | 0 | - |
| NO | Intact | 2.0 | 1.8 | 1.3 | 1.9 | 1.9 | 0.1 |
| | N+O | 1.2 | 0.3 | -1.4 | 2.5 | 1.5 | NS |
| NO | Intact | 1.8 | 1.7 | 1.1 | 1.9 | 1.6 | -0.1 |
| 100_2 | NO+O | 2.0 | 1.7 | 0.4 | 3.2 | 2.4 | NS |
| 0. | Intact | 1.6 | 0.9 | 0.2 | 1.2 | 1.8 | 0.3 |
| $ $ O_2 | 0+0 | 2.0 | 1.1 | -0.7 | 4.5 | 4.2 | -0.2 |
| N ₂ | Intact | 0.1 | 0.6 | 0.3 | 0.2 | 0.2 | 0.0 |

0). After each switch, the surface finds itself in a high-energy state and tries to reach its thermodynamic ground state, whose stoichiometry and structure can be predicted from first principles [213, 54, 217]. However, in the process of this evolution it must pass through the chemically active stoichiometric structures that we focus on in this work: we are in fact leveraging this surface evolution to drive the desired reactions. For example, as described above, the stoichiometric positively-poled surface dissociates O_2 and NO molecules and is driven to be saturated with strongly-bound O atoms: this O-rich surface is the thermodynamic ground state and is less chemically reactive. Switching to negative polarization then cleans off these O atoms (via O_2 formation and desorption): the surface becomes stoichiometric, which is again at or near its thermodynamic ground-state for negative polarization and is ready for the next polarization flip.

Table 6.2: Energy barriers in eV for key reactions on positively poled CrO_2 -PbTiO₃ and RuO₂-PbTiO₃. The energy barriers are defined as the energy difference between the transition state (located by NEB method with climbing image) and the adsorbed (chemisorbed) reactants state.

| Reaction | CrO_2 -PTO | RuO ₂ -PTO |
|----------------------|--------------|-----------------------|
| NO dissociation | 0.9 | 1.3 |
| O_2 dissociation | 0.0 | 0.0 |
| NO_2 dissociation | 0.5 | 0.0 |
| N_2 formation | 1.2 | 0.5 |
| $\rm CO_2$ formation | 1.6 | 0.8 |

6.3 NO_x direct decomposition via CrO_2 monolayer on PTO

Of course, there is no a priori reason why a monolayer of RuO_2 — quite far from bulk RuO_2 — is necessarily optimal. Hence, we optimize the choice of transition metal oxide monolayer in order to (i) minimize the NO dissociation barrier, (ii) maximize the NO reformation barrier, (iii) preserve the small N_2 formation and desorption barriers in the positive polarization state, while (iv) enhancing inertness in the negative polarization state to ensure maximum desorption power and deliver a pristine surface. We have considered a number of transition metals including Ru, W, Mo, Fe, Cr, Pt, Au and Cu. We find that, beginning from Ru, moving to the left or downward on the periodic table increases the interaction with NO and the O_2 formation barrier while decreasing the NO dissociation barrier, while moving to the right or upward has the opposite effect. Mo and W interact too strongly with the adsorbates, while Fe, Pt, Au and Cu interact too weakly. We find that Cr is optimal for our needs. Table 6.1 lists binding energies for the CrO₂-PTO surface. Positively poled CrO₂-PTO is highly active toward adsorbates while the negatively poled surface is almost inert. Unlike RuO₂-PTO, the ground state for NO in positive polarization is found to be dissociated into bound N and O atoms. Similarly, dissociated NO_2 (NO+O) is favored over the intact molecule in positive polarization (see Table 6.1) with a small dissociation

barrier as per Table 6.2 (the NO will further dissociate into N and O atoms). Figure 6.3.1 depicts the binding geometry of NO₂ to CrO₂-PTO and RuO₂-PTO. As one can notice, in both cases there is a significant charge transfer to the NO_2 antibonding LUMO (Fig. 5.3.2 shows HOMO, SOMO and LUMO for a collection of molecules). This makes the N-O bond longer (by 0.07, and 0.19 Å for CrO_2 -PTO and RuO_2 -PTO, respectively) and weaker and prepares it for dissociation $(NO_2 \rightarrow NO+O)$. Especially in the case of NO_2 on RuO_2 -PTO, one can see the formation of a covalent bond between the NO₂ LUMO and the surface Ru $4d_{xz}$ and Ru $4d_{yz}$ orbitals, which lowers the energy of the NO_2 LUMO and further enhances the electron transfer to this orbital. Formation of this covalent bond on RuO_2 -PTO, but not on CrO_2 -PT,O is thought to be the reason behind the lower NO_2 dissociation barrier on RuO_2 -PTO relative to CrO_2 -PTO (0.0 vs 0.5 eV). Eventually, the bound N and O atoms are converted to N_2 and O_2 in later steps of the cycle. Table 6.2 provides the key barriers on positively poled CrO₂-PTO: the NO dissociation barrier has been lowered compared to RuO_2 -PTO, the O_2 dissociation barrier is negligible, and the N_2 formation barrier is somewhat increased. We graphically illustrate our envisioned cycle in Fig. 6.3.2 showing how cyclical polarization switching of CrO₂-PTO can effectively catalyze NO direct decomposition into N_2 and O_2 . The energy landscape diagram of the cycle is depicted in Fig. 6.6.1, where we can see the progression of surface states and the quantitative changes in energy states, as well as the key transition states.

6.4 A search for optimum metal oxide monolayer for NO direct decomposition

As mentioned in the previous section, we believe that CrO_2 is the optimal monolayer for achieving our desired reactions for NO direct decomposition. This choice was arrived at after a survey of different transition metals including Ru, W, Mo, Fe, Cr,



Figure 6.3.1: Binding geometry and charge transfer (in RGB scale) for binding of 0.5 ML NO₂ to CrO₂-PTO (left hand side), and b) RuO₂-PTO (right hand side). N is shown in pale blue, O (red), Pb (gray), Ti (cyan) encaged in oxygen octahedra, Cr (magenta) and Ru (green). As indicated in the figure, color red shows regions of space populated by electrons, while blue regions show depopulation of electrons and the neutral background is shown by green. One can notice a charge transfer from the transition metal (Cr, Ru) d_{z^2} orbital to NO₂ antibonding LUMO, which elongates and weakens the N-O bond and prepares it for dissociation.

Pt, Au and Cu combined with a consideration of the trends among these results. The previous sections presented results for Cr and Ru, and here we present some of the other cases.

The general trend that was found was that beginning from Ru (our initial choice) and moving to the left in periodic table increases the interaction with NO (and O) while moving up in the periodic table decreases the interaction. This is correlated with the trend on transition metal surfaces, in which the interaction with adsorbates increases when the center of the transition metal d-band is closer to the Fermi energy (d-band model) [40, 300].



Figure 6.3.2: Proposed catalytic cycle on CrO_2 -PbTiO₃ for NO direct decomposition into N₂ and O₂. In each case, the polarization direction is indicated by gray arrows. The green arrows show adsorption and desorption of the molecules. The cycle begins with a clean and pristine positively poled surface and through multiple steps (after effectively dissociating 2 NO molecules into N₂ and O₂) returns to this state.

| WO ₂ -PbTiO ₃ | Polarization | Binding energy(eV) |
|-------------------------------------|--------------|--------------------|
| | Positive | 2.43 |
| NO intact binding | Paraelectric | 3.80 |
| | Negative | 1.90 |
| | Positive | 5.45 |
| NO dissociative binding | Paraelectric | 4.35 |
| | Negative | 0.31 |
| | Positive | 2.31 |
| O_2 intact binding | Paraelectric | 3.31 |
| | Negative | 2.15 |
| | Positive | 7.12 |
| O_2 dissociative binding | Paraelectric | 7.99 |
| | Negative | 2.03 |

Table 6.3: NO and O_2 intact and dissociative binding energies(eV) on WO₂-PbTiO₃. NS means the configuration is not mechanically stable.

6.4.1 WO₂ monolayers on PTO

Table 6.3 shows that WO_2 -PTO interacts too strongly with key adsorbates (e.g., the O_2 interaction with the surface is too strong for all polarizations). Hence, it is not appropriate for driving the desired NO direct decomposition reaction.

6.4.2 MoO₂ monolayers on PTO

Similar to WO_2 above, as Table 6.4 shows, MoO_2 -PTO also interacts too strongly with key adsorbates (e.g., the O_2 interaction with the surface is too strong for all polarizations). Hence, it is not appropriate for driving the desired NO direct decomposition reaction.

6.4.3 FeO₂ monolayers on PTO

As Table 6.5 illustrates, FeO₂-PTO does not interact strongly enough with key adsorbates: e.g., the NO dissociative binding mode on positive polarization is not strong enough.

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| MoO_2 -PbTiO ₃ | Polarization | Binding energy(eV) |
|-----------------------------|--------------|--------------------|
| | Positive | 2.54 |
| NO intact binding | Paraelectric | 2.63 |
| | Negative | 1.04 |
| | Positive | 4.96 |
| NO dissociative binding | Paraelectric | 2.19 |
| | Negative | -0.76 |
| | Positive | 2.05 |
| O_2 intact binding | Paraelectric | 1.89 |
| | Negative | 0.83 |
| | Positive | 6.58 |
| O_2 dissociative binding | Paraelectric | 4.87 |
| | Negative | 0.39 |

Table 6.4: NO and O_2 intact and dissociative binding energies (eV) on MoO_2 -PbTiO₃. NS means the configuration is not mechanically stable.

Table 6.5: NO and O_2 intact and dissociative binding energies (eV) on FeO₂-PbTiO₃. NS means the configuration is not mechanically stable.

| FeO ₂ -PbTiO ₃ | Polarization | Binding energy(eV) |
|--------------------------------------|--------------|--------------------|
| | Positive | 1.47 |
| NO intact binding | Paraelectric | 0.96 |
| | Negative | 0.45 |
| | Positive | 0.16 |
| NO dissociative binding | Paraelectric | -2.07 |
| | Negative | NS |
| | Positive | 1.42 |
| O_2 intact binding | Paraelectric | 0.18 |
| | Negative | 0.19 |
| | Positive | 1.79 |
| O_2 dissociative binding | Paraelectric | 0.30 |
| | Negative | -1.63 |
| AuO_2 -PbTiO $_3$ | Polarization | Binding energy(eV) |
|----------------------------|--------------|--------------------|
| | Positive | 0.85 |
| NO intact binding | Paraelectric | NS |
| | Negative | NS |
| | Positive | -4.12 |
| NO dissociative binding | Paraelectric | -1.84 |
| | Negative | NS |
| | Positive | 0.04 |
| O_2 intact binding | Paraelectric | 0.1 |
| | Negative | 0.02 |
| | Positive | -1.56 |
| O_2 dissociative binding | Paraelectric | -1.93 |
| | Negative | -1.25 |

Table 6.6: NO and O_2 intact and dissociative binding energies (eV) on AuO₂-PbTiO₃. NS means the configuration is not mechanically stable.

6.4.4 AuO₂ monolayers on PTO

The results in Table 6.6 for AuO_2 -PTO show that it interacts too weakly with the adsorbates (e.g., the NO dissociative binding mode on positive polarization is much less stable than NO in gas form).

6.4.5 PtO₂ and CuO₂ monolayers on PTO

For the cases involving Pt and Cu, we find that the NO dissociative binding mode is not even mechanically stable (separated N and O atoms recombine with zero barrier and form NO). Hence, they are readily ruled out as catalysts of interest for NO direct decomposition as part of a catalytic cycle.

6.5 CO oxidation via CrO₂ and RuO₂ monolayer on PTO

In addition to NO_x direct decomposition into N_2 and O_2 , both RuO_2 -PTO and CrO_2 -PTO can simultaneously oxidize CO into CO_2 . Table 6.9 shows that the O-rich positively poled surfaces oxidize CO into CO_2 , since a) CO has a strong interaction with the surfaces, b) CO_2 formation is favored over separated CO and O, and c) CO_2 formation barriers are modest in both systems (see Table 6.2). On RuO₂-PTO surfaces, CO_2 is released after formation (in positive polarization), while on CrO_2 -PTO CO_2 is released after switching to negative polarization where there is negligible surface-molecule interaction (see Table 6.1). As another surprising added benefit, this class of systems shows tolerance against sulfur poisoning, a significant challenge and an active area in emission control research [270, 269, 301, 302, 303, 304]. The binding energies in Table 6.9 for SO₂ and H₂O molecules are small in at least one polarization state: when the polarization is cycled, these molecules readily desorb and the surface does not become saturated (poisoned).

6.6 Switching the ferroelectric polarization

We conclude this section on the cyclic catalysis with some comments on two key rates in this system. First, the chemical reactions on the surfaces have energy barriers $\Delta \sim 1$ eV, which at a temperature of T = 600 K and assuming a pre-exponential prefactor of $\nu = 5 \times 10^{12}$ Hz in the transition state theory rate $\nu \exp(-\Delta/k_B T)$, gives order of magnitude estimate rates of $\sim 2 \times 10^4$ Hz. The second time scale is that time required to switch the ferroelectric polarization: electrically, this can be accomplished in existing systems with rates of $\sim 10^7 - 10^8$ Hz [305, 306]. Hence, the ferroelectric switching rate should not be a limiting factor for such a cyclic device, and we expect to derive the full benefit from the polarization enhanced catalytic activity.



Figure 6.6.1: Energy landscape diagram for the proposed catalytic cycle on CrO_2 -PbTiO₃ for NO direct decomposition into N₂ and O₂. The two arrows indicate the direction of the polarization in each part of the cycle: on the left is positive (up) polarization (parallel to the surface normal vector), while on the right is negative (down) polarization (antiparallel to the surface normal vector). The dashed gray line indicates the point in the cycle at which the polarization is flipped. Horizontal plateaus locate local minima, circles represent transition states as highlighted by the \ddagger label . The reference energy is that of two NO molecules in the gas phase above a 2×2 CrO₂-PbTiO₃ surface in positive polarization.

6.7 Stability of RuO_2 and CrO_2 monolayers on fer-

roelectric PTO

We now address basic aspects of the stability of these monolayers. We find that monolayers of RuO₂ and CrO₂ on paraelectric PTO can lower their energies via interdiffusion of Ru (Cr) atoms into the PTO as well as by lack of wetting (i.e., energetic preference to form bulk RuO₂ and CrO₂). However, once $P \neq 0$, the interdiffusion problem is overcome as it raises the total energy (see Table 6.7), but the wetting problem remains (see Table 6.8). One solution involves a simple modification where x unit cells of SrTiO₃ (STO) are inserted between the catalytic monolayer and the PTO, denoted as Ru(Cr)O₂-(STO)_x-PTO (see Fig. 6.7.1 and Tables 6.8 and 6.7). Our DFT results for x = 0 to x = 5 show that bulk oxide formation is suppressed by the presence of the STO buffer layer. Crucially, the polarization-dependent surface chemistry is unchanged (binding energies for x = 1-5 change at most by 0.3 eV per adsorbate compared to the x = 0 case), which stems from our finding that the Table 6.7: Stability (against interdiffusion) of a transition metal oxide monolayer on ferroelectric PbTiO₃. Our convention is that more positive numbers mean greater stability. In each case, several configurations in which some of the surface Ru (Cr) are interchanged with Ti below the surface are computed, the most stable structure is chosen, then the energy difference of this structure (interdiffused) with the original structure (perfect monolayer on top) is reported as the stability against interdiffusion.

| polarization | stability vs. interdiffusion on BuO ₂ -PTO (eV) | stability vs. interdiffusion on CrO ₂ -PTO (eV) |
|--------------|---|---|
| positive | 1.6 | 0.2 |
| paraelectric | -0.5 | -0.2 |
| negative | 0.4 | 0.5 |

Table 6.8: Stability (against bulk crystallite formation, i.e., bulk CrO_2 and bulk RuO_2) of a transition metal oxide monolayer on PbTiO₃. Our convention is that more positive numbers mean greater stability.

| Stability of top metal oxide monolayer vs. bulk crystallite formation | polarization | $ \begin{array}{c} \operatorname{CrO}_2 \text{ on top} \\ \left(\operatorname{eV} \right) \end{array} $ | $\begin{array}{c} \operatorname{RuO}_2 \text{ on top} \\ (eV) \end{array}$ |
|---|--------------|--|--|
| 0 lavor STO buffor | positive | -0.3 | 0 |
| | negative | 1.0 | -0.5 |
| 1 laver STO buffer | positive | 0.6 | 1.8 |
| | negative | 1.5 | 0.3 |
| 2 laver STO buffer | positive | 0.4 | 1.1 |
| | negative | 1.1 | 0.2 |
| 3 laver STO buffer | positive | 0.2 | 0.6 |
| 5 layer 510 buller | negative | 1.1 | 0.0 |

polarization propagates perfectly through the STO. This is because STO is a strongly polarizable incipient ferroelectric (quantum paraelectric) [307, 308] which is further aided by the strain enforced on it by the PTO to render it ferroelectric [309, 310]. With STO as a buffer layer we effectively have a monolayer of either SrRuO₃ or SrCrO₃ on the surface of the material. The fact that SrTiO₃, SrRuO₃, SrCrO₃ and PbTiO₃ are all experimentally known materials with lattice parameters within 3% of each other [311, 312, 313, 314, 315, 316, 317, 318] is also consistent with our prediction of the thermodynamical stability of the Ru(Cr)O₂-(STO)_x-PTO system with respect to formation of bulk RuO₂ and CrO₂ or interdiffusion in both polarization states.



Figure 6.7.1: A sample RuO_2 -(STO)₃-(neg)PTO system, in which a STO buffer layer is used to stabilize the transition metal oxide monolayer. The active surface transition metal (Ru, Cr, etc.) is shown by green, Ti is blue, oxygen is red, Pb is shown in gray and Sr is shown in cyan. The induced polarization of the substrate penetrates almost perfectly into the STO buffer layer; consequently, the surface chemistry is only minimally perturbed by the STO buffer layer.

Table 6.9: Polarization-dependent binding energies in eV for CO, CO₂, SO₂ and H₂O on RuO₂-PTO and CrO₂-PTO for positive, paraelectric and negative polarizations, indicated by (+), (0), and (-), respectively for 0.5 ML coverage. More positive numbers denote increased stability. Binding energies are relative to the energy of the gas phase molecule. NS means no mechanically stable configuration exists.

| Binding | Modo | RuO ₂ -PTO | | CrO ₂ -PTO | | | |
|------------------|--------|-----------------------|------|-----------------------|------|------|-----|
| Molecule | Mode | + | 0 | - | + | 0 | - |
| CO | Intact | 1.7 | 1.7 | 1.7 | 0.8 | 0.7 | 0.0 |
| CO- | Intact | 0.1 | 0.8 | 0.7 | 0.8 | 1.0 | 0.0 |
| | CO+O | -0.4 | -0.8 | -2.0 | -0.2 | -0.7 | NS |
| SO_2 | Intact | 0.3 | 0.9 | 0.4 | 1.3 | 0.6 | 0 |
| H ₂ O | Intact | 0.4 | 0.7 | 0.7 | 0.5 | 0.5 | 0.1 |

6.8 Electronic and structural basis of polarization dependent chemistry

We turn to electronic structure analysis to clarify the underlying physical basis of the striking polarization dependent chemistry. First, we examine how the oxidation state of the surface transition metal changes as a function of polarization. We provide evidence of the oxidation state change for the CrO_2 monolayer. First and most simply, the average Cr-O bond lengths in positive and negative polarizations are 1.94 and 1.69 Å, respectively. Since the Cr coordination number is unchanged, this correlates directly with increasing oxidation states [319] as expected from removal of electrons with decreasing surface charge ($\vec{P} \cdot \hat{n}$). Second, according to our calculations (using the Berry Phase method [53, 320]) and in agreement with the literature [182, 181], bulk PTO has a ferroelectric polarization magnitude of $P = 93 \ \mu\text{C/cm}^2$ that corresponds to a surface charge density of 0.87 electrons/Cr which must be compensated by addition or removal of electrons to the surface. As we show below, the electronic states at or near the Fermi energy have primarily Cr 3d character, so the added or removed electrons will be residing on the surface Cr sites. Given that the polarization profile is quite uniform in our films right up to the surface, we expect the full $\approx \pm 1$ change of electron number and hence oxidation number on each Cr with polarization reversal. Third, monitoring the magnetic moment of the surface Cr provides a more direct measure of the change of oxidation state. CrO₂-PTO is effectively a monolayer of perovskite $PbCrO_3$ on TiO_2 -terminated $PbTiO_3$. For bulk $PbCrO_3$, we find a large exchange splitting and a magnetic moment of $2\mu_B$ per Cr as per prior literature [321]: in both bulk PbCrO₃ and CrO₂, we have $Cr^{+4}(3d^2)$ with a large exchange splitting that aligns the two 3d electron spins. For CrO_2 -PTO, we compute magnetic moments of $3.1\mu_B$, $2.2\mu_B$ and $0.3\mu_B$ per Cr for positive, paraelectric, and negative polarizations, respectively. As expected, the paraelectric state agrees closely with the bulk (i.e., unchanged Cr^{+4} oxidation state). For positive polarization, the enlarged magnetic moment of $3.1\mu_B$ and the exchange splitting observed in the density of states (see Fig. 6.8.1) signal the high-spin $Cr^{+3}(3d^3)$ state. For negative polarization, we have $\operatorname{Cr}^{+5}(3d^1)$ which has negligible exchange splitting and is paramagnetic (see Fig. (6.8.1). We note that, unlike bulk PbCrO₃ which is a G-type antiferromagnet [322, 323, positively-poled CrO₂-PTO prefers ferromagnetism over antiferromagnetism and paramagnetism by 0.15 and 1.5 eV per Cr, respectively. Hence, CrO_2 -PTO shows a strong magnetoelectric effect: it is a paramagnet in negative polarization but a robust ferromagnet in positive polarization (other examples of ferroelectric control of spin polarization have been discussed in the literature. [324, 325, 326, 327, 328, 329, 330]). In brief, these results show that the polarization can shuttle $\approx \pm 1$ electron per surface transition metal, which modifies the oxidation state by $\approx \pm 1$ relative to paraelectric case and underpins the dramatic polarization dependent chemistry seen above.

After an extensive analysis, we find that the polarization-dependent surface electron count controls binding energies (Tables 6.1 and 6.9) via two separate channels: (i) charge transfer between the surface and adsorbates, and (ii) covalent binding between the adsorbates and surface. In most cases, both operate at once, but for simplicity we present two examples where one mechanism dominates: (a) charge transfer for O_2



Figure 6.8.1: Projected density of states (PDOS) on Cr 3d orbitals for CrO_2 -PbTiO₃ in positive and negative polarizations in spin up and down channels. Black lines are majority spin (up) PDOS and green lines are minority (down) PDOS. The red and blue horizontal lines mark the energies of the SOMO and LUMO states of the NO molecule in gas phase. Left: PDOS on Cr 3d in the ground state for negative polarization (Cr in oxygen tetrahedral cages as per Fig. 6.8.3a) we see a small exchange splitting that corresponds to one electron per Cr site. Center: PDOS on Cr 3d for the negatively poled surface that is ready for binding adsorbates (oxygen tetrahedral cage is broken as per Fig. 6.8.3d). Right: PDOS on Cr 3d states for the ground state of the positively poled surface, we see an enlarged exchange splitting that corresponds to existence of three electron per Cr site.

dissociative binding, and (b) covalent effects for NO intact binding.

Figures 6.8.2(a) and (b) show the binding configurations for O₂ dissociative binding on RuO₂-PTO. As Fig. 6.8.2(e) shows, the adsorbate O 2p state is 1.9 eV lower than the surface Fermi energy, hence the dominant effect is electron transfer from the surface to the oxygen adsorbates. The decrease of Ru oxidation state (by ~ 2 units) is visible as the enlarged occupation of, and increase in the density of, states of the Ru 4d-dominated conduction bands when changing the sign of P. Hence, there is more electron transfer to the low-energy states of the oxygen adsorbate, which greatly increases the binding energy by 2.7 eV per dissociated O₂ molecule.

Figures 6.8.2(c) and (d) show the binding configurations for NO adsorption on RuO_2 -PTO. As visible in Fig. 6.8.2, the tiny difference between the energy of the NO Singly Occupied Molecular Orbital (SOMO) and the Fermi energy of the surfaces obviates charge transfer, so covalent bonding between adsorbate and surface states is critical. To understand this, we generalize the well known d-band model for transition metal surfaces [42] in which the energy difference between the Fermi energy (E_F) and the center of the transition metal d band is a good descriptor for adsorption energies. In transition metal oxides, cation d states and O 2p states hybridize to form valence and conduction bands. However, in our systems (a) molecular binding occurs on the transition metal sites (e.g., Fig. 6.8.2), (b) the conduction bands are dominated by anti-bonding d states, and (c) E_F lies in or near the conduction band, so the obvious generalization is to consider the relative alignment of E_F with the center of the conduction band. Auxiliary reasons are that the portion of the d states that hybridize with O 2p orbitals forming bonding states (i) lie deep in the valence band (well below E_F) and do not contribute to adsorbate bonding, and (ii) tend to point in-plane or into the surface and have small spatial overlap with adsorbate molecular orbitals. Figure 6.8.2(e) highlights the alignment of the Ru 4d states with the NO SOMO and Lowest Unoccupied Molecular Orbital (LUMO). We compute the center of the conduction part of the d-band by integrating the shaded Ru 4d portion of the density of states in Fig. 6.8.2(e) and find that for P > 0 it is closer to the NO SOMO by 0.8 eV (E_F and the SOMO are energetically coincident). Hence, we believe that the energy difference between E_F and the center of the conduction band is a good descriptor of substrate-adsorbate interaction, especially when covalency is the dominant mechanism in the binding.

The CrO_2 -PTO system shows very similar behavior: for negative polarization, we have reduced electron density and an upward shift of the conduction band center relative to Fermi energy when compared to positive polarization, as per Fig. 6.8.1. As it can be seen in Fig. 6.8.1, the center of the conduction band for positively poled CrO_2 -PTO lies almost at E_F , but the center of the conduction band for negatively poled CrO_2 -PTO (which is prepared for molecular binding) lies 0.95 eV above the Fermi energy. This leads to a weaker covalent bond between the NO molecule and the surface in negative compared to positive polarization.

Tables 6.1 and 6.9 show that the negatively poled CrO_2 -PTO surface is strikingly inert to molecular interactions. The primarily reason for this behavior is geometrical. Figure 6.8.3(a) shows that for the ground-state of negatively poled CrO_2 -PTO, the Cr^{5+} ions are enclosed in distorted tetrahedral oxygen cages. The active electronic states on the surface, which are dominantly on the Cr, are thus inside the cage (see Fig. 6.8.3 (c)). To bind an adsorbate, a cage must break to expose a Cr as exemplified by Fig. 6.8.3(b), which then exposes electronic states at the Fermi level on the Cr to the adsorbate for covalent binding (see Figs. 6.8.3 (b) and (d)). Energetically, each cage breaking costs a penalty of 0.8 eV, destabilizing molecular binding significantly. This unusual behavior likely stems from two sources. First, Cr^{5+} has a single 3*d* electron so it prefers maximum local symmetry reduction and a lowest-energy nondegenerate electronic configuration. Second, Cr^{5+} has a relatively small size: we find that isoelectronic Mo^{5+} and W^{5+} do not form such tetrahedral cages. This correlates



Figure 6.8.2: Polarization-dependent binding geometries and electronic structure for RuO_2 -PbTiO₃. O₂ dissociative binding for a) negatively and b) positively poled and NO binding on c) negatively and d) positively poled RuO_2 -PTO. Atoms are Ti (dark blue), Pb (gray), O (red), N (pale blue), and Ru (green) [196]. e) Projected density of states on the surface Ru 4d atomic orbitals for negative and positively poled RuO_2 -PTO energetically aligned with molecular and atomic adsorbate states. Shaded regions highlight the Ru 4d-dominated conduction bands (for details, see Methods section).

to their larger ionic radii (Mo⁵⁺: 0.61 Å , W⁵⁺: 0.62 Å , Cr⁵⁺: 0.49 Å) so they likely do not fit inside a stable O^{2-} tetrahedral cage [319].

We conclude our analysis of electronic behavior by illustrating the redistribution of electrons in real space upon NO adsorption on positively and negatively poled CrO_2 -PTO and RuO_2 -PTO (see Figs. 6.8.4 and 6.8.5). On the positively-poled CrO_2 -PTO surface, one can see that there is a strong covalent bonding between Cr and NO: electrons occupy a bonding state that is a hybrid of the NO SOMO, Cr $3d_{xz}$ and Cr $3d_{yz}$ states. The states near the edge of the conduction band on the surface Cr atom are made of $3d_{xz}$, $3d_{yz}$, $3d_{xy}$ and $3d_{3z^2-r^2}$ orbitals, but the last two do not interact with the NO SOMO which has π character: the d_{xy} orbital points in plane while the $d_{3z^2-r^2}$ has zero total overlap with NO SOMO by symmetry. Hence, we expect electron transfer from Cr $3d_{xy}$ and $3d_{3z^2-r^2}$ orbitals to the lower energy bonding combination of the NO SOMO and Cr $3d_{xz} + 3d_{yz}$ states, which is visible in Fig. 6.8.4. A covalent bonding of a similar form also takes place on the negatively poled CrO₂-PTO surface, but for the reasons described above, the binding energy and the covalency are much smaller. Similar to CrO_2 -PTO, as it can be seen in Fig. 6.8.5 the polarization direction controls the extent of covalent bonding between NO and surface Ru on RuO₂-PTO.

6.9 Computational Methods

6.9.1 Convergence parameters, supercell and exchange correlation functional

We perform first principles spin-polarized density functional theory (DFT) calculations [331, 10] with a plane-wave basis set using the Quantum Espresso software [172] and ultrasoft pseudopotentials [173, 174, 175]. We use PbTiO₃ (PTO) as the oxide



Figure 6.8.3: Breaking of the oxygen tetrahedral cages upon molecular binding and exposure of Cr 3d states. Surface of negatively-poled CrO_2 -PTO a) without NO and b) with NO adsorbed. c) Local density of states at the Fermi level (yellow isosurfaces) for the ground-state structure of negatively poled CrO_2 -PTO: the density is localized primarily on the Cr inside the oxygen tetrahedral cages. d) Local density of states at the Fermi level for the negatively poled CrO_2 -PTO surface with broken oxygen cages and hence exposed Cr that is ready for binding adsorbates. The atoms are: Cr (pink), O (red), Pb (gray), and Ti (blue).



Figure 6.8.4: Real space electron redistribution shows covalent bond formation upon NO adsorption on the surface Cr atom for a) positively poled and b) negatively poled CrO₂-PTO. Blue isosurfaces show regions in space that are depopulated by electrons, while red isosurfaces show the regions that get populated by electrons when NO binds to the surface Cr. In a) there is strong covalency between the NO and Cr, thus the state becoming occupied is a bonding combination of the NO SOMO (π symmetry) and the surface Cr $3d_{xz}$ and Cr $3d_{yz}$ orbitals. In b) the covalency is weaker.

ferroelectric and employ a slab geometry with the (001) direction for the surface normal and the polarization axis. We introduce at least 15 Å of vacuum on top of the surface in our unit cell. A dipole correction in the center of the vacuum is used in order to eliminate the artificial electrical field and the unphysical dipole-dipole interactions among the copies of the slab in the z direction [176]. We use a kinetic energy cut off for wave functions (E_{cut}) equal to 30 Ry, and a sampling for k space equivalent to $8 \times 8 \times 8$ sampling for a 1×1 cell. The smearing scheme for the Kohn-Sham orbitals' occupations is the cold smearing of Marzari and Vanderbilt with a temperature equal to 2 mRy/k_{B} [177]. All convergence parameters are chosen to yield binding energies better than 0.1 eV.

We use a standard method whereby a few layers of Pt are placed on the bottom PTO surface to create an electrode and a large density of states at the Fermi level: this simulates an electron reservoir that exists in a realistic system with a thick



Figure 6.8.5: Real space electron redistribution upon NO adsorption for a) positively and b) negatively poled RuO_2 -PTO. Blue isosurfaces show regions in space that are depopulated by electrons, while red isosurfaces show the regions that get populated by electrons. N is shown in pale blue, O (red), Pb (gray), Ti (cyan), and Ru (green). As one may notice, there is a stronger covalent bonding between NO and positively poled surface as a result of a more favorable band alignment than negatively poled surface.

ferroelectric film [54, 180, 178, 179]. It should be noted that the Pt layers have a small enough lattice mismatch (< 4%) with the PTO slab so as not to introduce any artificial interface effect on the bottom PTO surface. We fix the structure of the second, third and fourth atomic layers of PbTiO₃ on top of the Pt electrode to their bulk values in order to help simulate the mechanical boundary conditions appropriate to a thick PbTiO₃ film: this leads to reasonable computational expenses and sizes of the simulation cells [54, 179, 332, 333, 334, 335].

Our tabulated results employ the PW91 GGA exchange-correlation (XC) functional [336, 13] but changing the XC functional to PBE GGA changes binding energies by less than 15%, and this does not affect our main results and conclusions. We have also performed extensive DFT+U calculations of our surface systems as tabulated in the following subsection. However, the physically appropriate value of the Hubbard U parameter for both CrO_2 -PTO and RuO_2 -PTO systems is quite small (i.e., weak electronic correlations). Hence, our GGA results should be in better agreement with experiment than GGA+U results with moderate or large U values.

In more detail, in DFT+U theory, U is a semiemperical parameter typically determined by comparing computed results with experiments and choosing the U that yields the best agreement [337, 338, 339, 340, 341]. In our case, the closest experimentally available systems are are CrO_2 and RuO_2 . In 2005, Toropova *et al.* showed that CrO_2 is in fact a weakly correlated material and even relatively small values of 1-2 eV for U fail to describe its magnetic properties correctly [342]. We have also confirmed this in our own U = 0 GGA calculations for CrO_2 which we find to be a half metallic ferromagnetic material with 2 μ_B per Cr in the rutile structure with lattice parameters a = 4.43 Å and c/a = 0.6587, which is in excellent agreement with experimental values [343]. The agreement of the computed structural properties with experiment systematically worsens as U is increased in our GGA+U calculations. Next, RuO_2 (110) surface chemistry has been the subject of numerous theoretical and experimental studies [297, 298, 344, 345, 346]. It has been shown that binding energies calculated by GGA are in very good agreement with the experimentally observed values [297]. We find the same to be true and that increasing U systematically worsens the agreement. Separately, we have used the first-principles linear response approach [347] to estimate U and find values of 3.6 and 4.7 eV for CrO_2 and RuO_2 , respectively. Unfortunately, these large U values do not provide the best agreement with available experiments. Hence, we conclude that using U = 0 for both the RuO₂-PTO and CrO₂-PTO systems should yield the most realistic results for binding energies.

6.9.2 Benchmarking with experimental data

In order to benchmark our PW91 GGA results for binding energies, we compare our results for CO and NO binding to $RuO_2(110)$ with experimental and theoretical values in the literature [297]. For 1 ML CO adsorption, we find a binding energy of 1.3 eV which is in good agreement with the values 1.0 and 1.18 eV obtained by experiment and PBE GGA, respectively. For 1 ML NO adsorption, we find a binding energy of 1.7 eV which is in good agreement with the values 1.34 and 1.61 eV obtained by experiment and PBE GGA, respectively [297].

6.9.3 Calculating the energy barriers

In order to calculate the energy barriers between local minima, we use the Nudged Elastic Band (NEB) method with climbing images [18, 19, 20, 348, 349, 21, 350], variable elastic constants ($\frac{k_{max}}{k_{min}} = 3$), and 6-8 images. In our NEB calculations, we permit the atoms in the top 2-3 atomic layers of the surface to move and fix the positions of all remaining atoms. We have checked that this introduces an error no more than 0.1 eV in the energy barriers.

6.9.4 Errors in finding the center of the bands

The shaded regions of the densities of states in Figs. 6.8.1 and 6.8.2(e) highlight the Cr 3d and Ru 4d-dominated conduction bands of the systems. Focusing on the Ru case as an example, the lower edge of the conduction band is clearly visible since the Ru 4d density of states shows a sudden and steep increase. We find that locating the precise numerical value for the lower edge is subject to a small uncertainty of ± 0.2 eV. This in turn leads to an uncertainty of no more than ± 0.02 eV for the center of the conduction band and ± 0.04 for the electron count per 1x1 cell on the surface. Similar results are found for Cr.

6.9.5 DFT+U calculations for RuO₂-PTO and CrO₂-PTO surface systems

We have performed a number of PW91 GGA+U calculations for our transitional metal oxide monolayer systems on ferroelectric substrates. As explained above, the physically appropriate value of the Hubbard U parameter for both CrO_2 -PTO and RuO_2 -PTO systems is most likely to be small or zero (i.e., weak electronic correlations). Hence, we believe that GGA results should be in better agreement with experiment than GGA+U results with moderate or large U values. In Tables 6.10 and 6.11 we present representative GGA+U results for binding energies in eV for two key adsorbates of interest to us: NO and O₂ binding to RuO_2 -PTO and CrO_2 -PTO surfaces. In general, we see systematic trends in the changes of binding energies with U. However, the desired chemical behavior we rely on in our cyclic catalytic scheme described in the main text is preserved for U = 1 or 2 eV. Specifically, they are the findings that:

- 1) NO interacts strongly with positively polarized surfaces.
- 2) NO dissociative binding is strong and stable for positive polarization.
- 3) O_2 prefers to dissociate to O atoms for positive polarization.

4) For negative polarization, two separated O atoms favor forming O_2 ; O_2 interacts weakly with the surfaces; and O_2 is readily desorbed thereby leaving a pristine surface ready for the next polarization cycle.

6.10 Outlook and conclusions

The above theoretical results highlight the promise of this class of catalysts when operated in a cyclical fashion. However, cyclically switching the ferroelectric polarization is experimentally challenging. We mention some alternative ideas that may alleviate this difficulty. First, as the Table 6.1 indicates, the $CrO_2 - PTO$ system

| CrO ₂ -PTO | Polarization | U=0 (eV) | U=1 (eV) | U=2 (eV) |
|----------------------------|--------------|----------|----------|----------|
| | positive | 1.91 | 1.56 | 1.46 |
| NO intact binding | paraelectric | 1.91 | 1.68 | 1.30 |
| | negative | 0.12 | 0.02 | -0.02 |
| | positive | 2.53 | 1.69 | 1.16 |
| NO dissociative binding | paraelectric | 1.53 | 1.08 | 0.59 |
| | negative | NS | NS | NS |
| | positive | 1.20 | 1.28 | 1.26 |
| O_2 intact binding | paraelectric | 1.80 | 1.50 | 0.78 |
| | negative | 0.16 | -0.06 | -0.07 |
| | positive | 4.48 | 3.79 | 3.28 |
| O_2 dissociative binding | paraelectric | 4.19 | 3.73 | 3.17 |
| | negative | -0.16 | -0.31 | -0.40 |

Table 6.10: DFT+U calculations for NO and O_2 binding on CrO_2 -PbTiO₃. NS means the configuration is not mechanically stable.

Table 6.11: DFT+U calculations for NO and O_2 binding on RuO_2 -PbTiO₃.

| RuO ₂ -PTO | Polarization | U=0 (eV) | U=1 (eV) | U=2 (eV) |
|----------------------------|--------------|----------|----------|----------|
| | positive | 2.03 | 1.87 | 1.76 |
| NO intact binding | paraelectric | 1.84 | 1.86 | 1.86 |
| | negative | 1.28 | 1.26 | 1.25 |
| | positive | 1.22 | 1.08 | 0.65 |
| NO dissociative binding | paraelectric | 0.27 | 0.21 | 0.13 |
| | negative | -1.36 | -1.35 | -1.32 |
| | positive | 1.58 | 1.44 | 1.16 |
| O_2 intact binding | paraelectric | 0.88 | 0.79 | 0.69 |
| | negative | 0.18 | 0.14 | 0.10 |
| | positive | 1.98 | 1.80 | 1.47 |
| O_2 dissociative binding | paraelectric | 1.14 | 1.03 | 0.89 |
| | negative | -0.73 | -1.10 | -1.18 |

has very similar behaviors in paraelectric and positive polarizations. Thus one can cycle between paraelectric and negative polarizations. This can be achieved by using temperature. As long as the material can be engineered to prefer negative polarization at low temperatures, raising the temperature near the Curie point should render the system paraelectric. In this scenario, the rate limiting step in simultaneous NO_x direct decomposition and CO oxidation is NO dissociation on the paraelectric surface with a 1.6 eV barrier, which is still reasonably low given that we are operating near the Curie temperature (Curie temperature of bulk $PbZr_xTi_{1-x}O_3$ can be higher than 600 K [351, 157]). Second, as described above, $CrO_2 - PTO$ shows a strong magnetoelectric effect, so that one could employ magnetic fields to switch the polarization [94]. Third, ferroelectric thin films can sport adjacent domains of opposite out-of-plane polarization whose size and pattern can be experimentally controlled and preserved up to high temperatures $(785^{\circ}C)$ [352, 353, 354]. Under appropriate conditions, one can imagine that reactions proceed on the positive domains and the buildup of products eventually causes their diffusion onto the adjacent negatively poled regions where the remainder of the reactions take place. This approach requires control over the domain structure and reaction conditions but avoids the need to actually cycle the polarization. These suggestions are simply provided as potential avenues of exploration: whether and how the polarization should be cycled is fundamentally an experimental challenge. We hope this work will stimulate experimental interest in addressing these problems in order to study and exploit the potential of these catalytic oxide monolayers on ferroelectrics.

In conclusion, we have described catalytic systems consisting of a transition metal oxide monolayer on a ferroelectric oxide substrate. We propose that cycling between positive and negative polarization states of the ferroelectric makes these monolayers display catalytic behaviors that avoid the familiar compromises stemming from the Sabatier principle. A CrO_2 monolayer is an optimized choice for simultaneous NO_x



Figure 6.10.1: NO_x direct decomposition and CO oxidation on CrO_2 -PTO via a catalytic cycle driven by dynamically and periodically controlling the ferroelectric PTO polarization.

direct decomposition (a long-standing challenge in the automotive industry) and CO oxidation (Fig. 6.10.1). Moreover, this system has tolerance toward sulfur and water poisoning. In addition to promising surface chemistry, CrO_2 -PTO shows interesting magnetic and structural features, including magnetoelectric effects and major surface reconstructions in negative polarization. We also show that inserting SrTiO₃ buffer layers between the ferroelectric PbTiO₃ and the monolayer helps the monolayer wet the surface and avoid transition metal interdiffusion while not modifying the desirable surface chemistry. The scheme described in this work is general and, in principle, can be applied to and optimized for other chemical reactions. If experimentally feasible, this method can expand the range of catalytically active elements to those which are not conventionally considered for catalysis and might be more effective and economical, e.g., Cr instead of canonical precious metal catalysts for simultaneous NO_x direct decomposition and CO oxidation.

Chapter 7

Future Research Directions and Outlook

As mentioned earlier in Chapter 3, ferroelectrics offer several avenues for tackling some of the fundamental challenges in the field of heterogeneous catalysis. This can concern the circumvention of the scaling relations (or designing materials with better scaling relations) or overcoming some of the more fundamental aspects of conventional methods of catalysis i.e., the Sabatier principle. In the last three chapters, we showed how creating a cyclic system driven by the modulations of ferroelectric polarization can bring us beyond the limits of the Sabatier principle and let us design catalysts for reactions considered as challenging (if not impossible) in heterogeneous catalysis e.g., NO_x direct decomposition or thermal water splitting (thermolysis).

In the final chapter, we present preliminary results on two fronts: a) circumventing scaling relations using ferroelectric supports, and b) using cyclic polarization modulation to achieve methane partial oxidation to methanol. We believe these topics can be promising and rewarding future research paths.

7.1 Circumventing scaling relations using ferroelectric supports

As mentioned in Chapter 3, the need for an "extra degree of freedom" that can free us from the restrictions caused by scaling relations is one of the great challenges of catalysis. In Chapter 5, we mentioned that the existence of a parallel binding mechanism (charge transfer), in addition to covalency between the adsorbate and the surface (which is the normal mechanism of binding on transition metal surfaces) can remove the usually tight coupling between the dissociated binding state and transition state (TS) electronic structure. We think this can be a promising observation, and our conjecture is that the surface charge induced by the ferroelectric polarization might indeed be able to play the role of an "extra degree of freedom". In order to verify this conjecture, we need to study this effect in more detail, enlarge our database of materials, facets, and adsorbates, and obviously we need to investigate the correlation between the TS, intact and dissociated binding energies in this database.

A preliminary step we have already taken is to look at the effect of the ferroelectric support on the scaling relations of an ultrathin transition metal layer deposited on it. We are aware of the fact that theory and experiment both confirm that growing transition metals as ultrathin layers on ferroelectric oxides is a daunting task [285, 287, 355]. Although one might be able to kinetically trap this ultrathin layer for a finite amount of time [355], eventually the system finds its ground state, which is to form bulk transition metal crystallites on the oxide, which almost completely screens the effect of the underlying ferroelectric polarization. Nevertheless, we believe this is a useful gedanken simulation that can determine and isolate the extent to which the ferroelectric polarization can change the surface scaling relations. If the effect is found to be significant, one can design systems that do not suffer from this thermodynamic instability problem.



Scaling relations among binding energies of different adsorbate species on transition metal surfaces

Figure 7.1.1: Scaling relations for adsorbates binding to a set of 7 transition metal (001) surfaces: Pd, Rh, Ag, Pt, Mo, Nb and W. Binding energies are calculated using PBE-GGA XC and follow the convention used used throughout this work where more positive numbers indicate stronger bonding.

Figure 7.1.1 depicts the scaling relations among some adsorbates on the (001) surface of a small set of transition metals (see Fig. 3.2.3 for a bigger data set). Figure 7.1.2, on the other hand, shows the scaling relations on these metals once an ultrathin film of each is deposited on the polar (001) surface of ferroelectric PTO. It can be seen that scaling relations are a function of both thickness of the transition metal film and polarization direction. This figure confirms our conjecture that polarization-induced surface charge can act as an "extra degree of freedom" and change the regular scaling relations. The effect is most pronounced in the case of 1 ML transition metal deposition, in which the screening effect of the transition metal is minimized.

The fact that polarization direction (and magnitude) can change the scaling relations of ultrathin metallic layers deposited on the ferroelectric support can be considered as good news for catalysis. Hence, one can now try to design systems which not only benefit from the (switchable) induced surface charge (from the ferroelectric polarization) but also are thermodynamically more stable. We believe that using ultrathin transition metal oxides rather than ultrathin transition metal films might overcome the thermodynamic instability (as mentioned in Chapter 6). Clearly, studying scaling relations on transition metal oxide ultrathin films on ferroelectric supports, along



Figure 7.1.2: Scaling relations for adsorbates on ultrathin transition metals supported on (001) PbTiO₃ ferroelectric substrate. In making this data set, seven different transition metals were used: Pd, Rh, Ag, Pt, Mo, Nb and W. Binding energies are calculated using PBE-GGA XC. It can be seen that in the case of a monolayer of transition metal on PTO, polarization direction can significantly change the scaling relation.

with understanding the mechanism behind this change in scaling relations induced by ferroelectric supports, is one of the projects in our future research agenda.

One should also note that using ferroelectrics is not the only way to create an electric polarization close to the surface (which can induce extra holes or electrons to the surface). In 2014, Bai et al. studied Pt overlayers on Pd [195]. Here the difference in the work function of the two metals leads to creation of an electric polarization vector close to the surface at the Pt/Pd interface. Bai et al. showed that decreasing the thickness of the Pt overlayer enhances the hydrogen evolution reaction (HER) on these surfaces, and they correlated this with a more effective polarization induced charge transfer to the surface for smaller thicknesses. Thus, one can also envisage using overlayers of transition metals on other transition metals as a potential means to change the scaling relations, without undermining the surface stability. Another pathway might be to use promoters, e.g., alkali metals, to induce the surface charge and tune the scaling relations. In fact, the use of alkali (oxide) promoters has been experimentally known and implemented in refined catalysts used in industry for decades [1, 356].

7.2 Using ferroelectrics for direct partial oxidation of methane to methanol

Methane (CH₄) is the major constituent of natural gas, which is currently the cheapest source of hydrocarbons. Developing a catalyst for the direct conversion of methane to (more valuable) methanol has been one of the major challenges in chemistry over the last decades [47, 357, 358, 359, 360, 361, 362, 363, 364, 50, 365] and it has even been named "a holy grail in catalytic sciences" [366]. As we mentioned in Chapter 5, a ferroelectric surface under hole doped conditions (polarization vector pointing into the surface) is oxidizing, and this oxidizing property can be tuned depending on the extent of the polarization. On the other hand, under the opposite polarization (polarization vector pointing outward), the surface becomes reducing. Such a switchable oxidizing/reducing behavior is evident in Table 7.1.

In Chapter 5, we proposed a cycle of two polarizations in which the reducing properties of positive polarization was used to reduce (thus decompose) the NO molecule, and the negative polarization was used to oxidize (thus desorb) the adsorbed oxygens (left from NO decomposition). In Chapter 5, we also mentioned that this reducing/oxidizing cycle one can convert SO₂ to SO₃ efficiently $(SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g))$ is the rate limiting step in industrial sulfuric acid production thus a technologically important process). Now the question is whether we can use the same principle to design a direct partial oxidation catalyst to convert methane to methanol. In such a cycle methane can react with the oxidizing (negatively poled) surface to produce methanol (taking away 0.5 ML of the surface oxygen atoms). Then, one can switch the polarization to positive (reducing properties). As mentioned in chapter 5, oxygen molecules can dissociate very efficiently on this surface (0.0 eV barrier in our calcula)tions, which is for a substrate with P $\approx 120 \frac{\mu C}{cm^2}$), and replenish the missing oxygens and make the surface ready to go through the oxidizing phase again (upon switching) in which the methane can be converted to methanol again. The overall effect of such an oxidizing/reducing cycle will be direct partial oxidation of methane to methanol $(CH_4(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(g)).$

One can envisage the oxidizing/reducing cycle described above on both a) bare ferroelectrics (as exemplified by the approach in Chapter 5) and b) transition metal oxide terminated ferroelectrics (as exemplified by the approach in Chapter 6). The simpler and less computationally expensive approach is to use bare ferroelectrics. Below we present our results that examine the possibility of using bare ferroelectric PTO to catalyze partial oxidation of methane to methanol.

Table 7.2 shows the polarization dependent interaction between the methane

Table 7.1: Polarization dependent atomic oxygen binding energy and oxygen vacancy formation energy (in 0.5 ML coverage) on stoichiometric Pb terminated PbTiO₃. In a positively polarized sample, the oxygen vacancy formation cost is too high, while oxygen atoms bind strongly to the surface (reducing properties). In a negatively poled surface, both oxygen vacancy formation and atomic oxygen binding energies are negative (relative to O in O₂ molecule in gas); this means the stoichiometric surface not only desorbs oxygen atoms, but tends to give away (0.5 ML) of its stoichiometric oxygen content (oxidizing properties).

| Delegization | oxygen vacancy | atomic oxygen binding | |
|--------------|-------------------------|-----------------------|--|
| Folarization | formation energy (eV) | energy (eV) | |
| positive | 3.9 | 3 | |
| paraelectric | 3.7 | -0.7 | |
| negative | -0.7 | -0.7 | |

Table 7.2: Polarization dependent binding energies for CH_4 and O_2 on stoichiometric Pb terminated PbTiO₃. The oxidizing negatively poled surface interacts strongly with CH_4 (forming CH_3OH), while the reducing positively poled surface interacts strongly with oxygen molecules (dissociating O_2 into adsorbed oxygen adatoms). CH_3OH molecules weakly physisorb to the negatively poled surface (~0.1 eV per molecule) after formation, thus can be easily taken off the surface. Energies are relative to the molecules (CH_4 and O_2) in gas form.

| Polarization | CH_4 binding energy (eV) | O_2 binding energy (eV) |
|--------------|--------------------------------------|---------------------------|
| positive | 0.0 (intact) | 2.6 (dissociated) |
| paraelectric | 0.0 (intact) | 0.2 (intact) |
| negative | 1.7^* (forming CH ₃ OH) | 0.0 (intact) |

(CH₄) molecule and stoichiometric Pb-terminated PTO. Here, one can see that positively poled (reducing) surface does not interact with the CH₄ molecule, while the negatively poled (oxidizing) surface interacts strongly with CH₄ and oxidizes it to CH₃OH. We compute the energy barrier for this reaction (using the NEB method) to be ≈ 1.1 eV. Thus, in principle, one might think a PTO surface under cycling polarization condition can convert an intake of CH₄ and O₂ to CH₃OH, by direct partial oxidation of CH₄ in negative polarization. The cycle would use the surface unstable oxygen (as indicated in Table 7.2) and replenishes the surface oxygen reservoir by reducing oxygen molecules in positive polarization.

In principle, there are two problems that might hinder the cycle described above:

a) the produced CH_3OH (in negative polarization) might dissociate back to CH_4 and O on the positively polarized surface, and b) the unstable surface oxygen might find kinetically more favorable pathways to leave the surface. We have investigated both of these potential challenges. Regarding the first problem, CH_3OH prefers (by 1.6 eV per molecule) to be dissociated back to $(CH_4 + O)$ on the reducing positively polarized surface, as the intact binding energy is calculated to be 0.4 eV, while the dissociated binding mode energy $(CH_4 + O)$ is calculated to be 2.0 eV. Nevertheless, the dissociation barrier is calculated to be ≈ 2.0 eV, which means that although thermodynamics favors CH_3OH to dissociate back to $(CH_4 + O)$ on this surface, the kinetics plays a role in our favor and inhibits this reaction (since this process is very slow compared to the barrierless O_2 dissociation process which oxidizes the surface and brings it to thermodynamically stable and inert state with 0.5 ML O adsorbed before it can dissociate any CH_3OH back to CH_4 and O). Regarding the second problem, unfortunately, the kinetics plays a negative role here: as mentioned in Chapter 4, there is a pathway with smaller barrier (0.4 eV) for the unstable surface oxygen on the negatively polarized surface to directly find each other and leave the surface, which requires less activation than the pathway in which CH_4 is partially oxidized

Thus this simplest scheme of using bare ferroelectric PbTiO₃ polarization cycling to partially oxidize CH_4 into CH_3OH turns out to be ineffective due to unfavorable kinetics. However, we believe there is still room for future effort and research on this subject. One strategy, mentioned earlier, is to use monolayers of transition metal oxides on ferroelectric supports. Here one is still able to switch the surface between oxidizing/reducing modes using polarization modulation, but one can also try to search for a transition metal monolayer which can increase the direct O₂ formation barrier on negative polarization so that the partial oxidation process requires less activation than direct O₂ formation. This is a search and optimization problem

into CH_3OH with a 1.1 eV barrier.

which might turn out to be extremely rewarding, since it has the potential to unveil an efficient direct partial oxidation process for methane for the first time.

7.3 Conclusions and outlook

In the last few chapters we discussed the promising role that ferroelectrics can play in solving some of the challenges facing the catalysis community. We offered specific examples of using ferroelectric switchable surface chemistry to design catalytic processes that are not bound by the limits of the Sabatier principle, and to catalyze reactions that are considered challenging for heterogeneous catalysis, e.g., including thermal water splitting and NO_x direct decomposition. Another important possibility is to manipulate the surface scaling relations and improve the efficiency of catalytic processes. In this chapter we offered some examples of how using ferroelectrics can circumvent scaling relations in a specific class of materials (ultrathin transition metals on ferroelectrics). Further efforts in this direction might extend these results to more thermodynamically stable systems and increase our understanding of fundamentals of scaling relations and how to break away from them. We also investigated the possibility of using ferroelectrics to achieve "the holy grail in catalytic sciences", i.e., partial oxidation of methane to methanol. Our results point to potential future research in this direction.

In summary, the wealth of phenomena and the coupling among surface chemistry, a bulk order parameter (polarization), and external fields (including electric, magnetic, strain and temperature) make ferroelectrics very promising candidates for incorporation in future catalytic materials. Based on our work, we believe the most interesting behaviors of these materials that contribute significantly to catalysis are achieved in a dynamic and non-equilibrium mode: under switching polarization or constant perturbations by external fields. We hope our work motivates researchers, especially experimental scientists to help undertake the challenge of implementing the dynamic properties of ferroelectrics in catalysis. This may turn out to be a rewarding endeavor that could, in principle, lead to a leap forward for energy harvesting and efficient catalytic production of useful materials with significant benefits for humanity and our fragile environment.

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