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Exploring the complexity of nanostructured catalysts with computational chemistry methods

Pablo Castro Latorre



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**Exploring the complexity of nanostructured catalysts
using computational chemistry methods**

*Exploració de la complexitat de catalitzadors nanoestructurats
emprant mètodes de química computacional*

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Abstract

Heterogeneous catalysis relies on interactions with a material's surface to lower the energy barrier of chemical reactions, thus increasing their rate. Enhancing catalytic performance typically involves nanoscale surface modifications designed to increase the density of active sites and tailor their geometric and electronic structures at the atomic level, thereby optimizing adsorption energies, reaction intermediates stabilization, and turnover frequencies. However, the structural complexity of nanostructured multi-component catalysts precludes their understanding and rational improvement.

The work presented in this thesis studies different types of technologically relevant nanostructured ceria-based catalysts varying in shape, composition, size and dimensionality. Computational simulations are used to understand the effect of the interaction of different nanostructures with CeO_2 surfaces and elucidate their physical and chemical properties.

First, metallic Pt clusters supported on CeO_2 are studied to address the effects of electron transfer between metal particles and reducible oxides (known as Electronic Metal Support Interactions - EMSI) on the chemical properties of a Pt_8 cluster. A computational strategy is proposed and critically evaluated to systematically characterize the electron transfer process and the different possible resulting electronic states. The chemical properties of the different sites and electronic states of the supported Pt_8 cluster are evaluated, revealing significant effects in calculated adsorption energies due to EMSI for various reactants and intermediates.

Second, the structural and electronic properties of the interface between a 2D FeO monolayer and the $\text{CeO}_2(111)$ surface are investigated. Simulations reveal a corrugated interfacial geometry, structure, consistent with experimental observations of periodic nanostructures. The electronic structure analysis indicates the presence of multiple electronic states, exhibiting an intricate interplay between the $\text{Fe}^{2+}/\text{Fe}^{3+}$ - $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couples. These calculations also reveal the importance of dispersion interactions and oxygen adsorption in the stabilization of periodic FeO_x 2D nanostructures.

Finally, the chemical reactivity of an oxidized Pt_6O_9 cluster supported on CeO_2 is investigated to rationalize the high catalytic activity of oxidized ceria-supported Pt particles towards the CO oxidation reaction below room temperature. Activation energies of CO oxidation on the Pt_6O_9 cluster suggest that both the oxidized cluster and gas-phase O_2 are the main sources of O atoms for CO_2 formation. A reaction mechanism is proposed for the reaction on the Pt_6O_9 cluster

where the CeO₂ support acts as a spectator for the described catalytic cycles. Kinetic Monte Carlo simulations show the proposed mechanism to be consistent with high catalytic activity of Pt oxide clusters below room temperature.

Keywords

Heterogeneous catalysis; Cerium oxide; Density Functional Theory; Metal-Support Interactions

Resum en català

La catàlisi heterogènia es basa en les interaccions amb la superfície d'un material per reduir la barrera energètica de les reaccions químiques, incrementant així la seva velocitat. Millorar el rendiment catalític normalment implica modificacions a escala nanoscòpica de la superfície, aquestes són dissenyades per augmentar la densitat dels centres actius i ajustar les seves estructures geomètriques i electròniques a escala atòmica, optimitzant així les energies d'adsorció, l'estabilització dels intermediaris de reacció i el nombre de recanvi. No obstant això, la complexitat estructural dels catalitzadors nanoestructurats multicomponents dificulta la seva comprensió i millora racional.

El treball presentat en aquesta tesi estudia diferents tipus de catalitzadors nanoestructurats tecnològicament rellevants basats en cèria, amb diverses formes, composicions, mides i dimensionalitat. S'empren simulacions computacionals per comprendre l'efecte de la interacció de diferents nanoestructures amb superfícies de CeO_2 i per determinar-ne les propietats físiques i químiques.

En primer lloc, s'estudien clústers metàl·lics de Pt suportats sobre CeO_2 per analitzar els efectes de la transferència electrònica entre partícules metàl·liques i òxids reduïbles (coneguts com a Interaccions Electròniques Metall-Suport - EMSI) sobre les propietats químiques d'un clúster de Pt_8 . Es proposa i s'avalua críticament una estratègia computacional per caracteritzar sistemàticament el procés de transferència electrònica i els diferents estats electrònics resultants possibles. S'avaluen les propietats químiques dels diferents centres actius i estats electrònics del clúster de Pt_8 suportat, denotant efectes significatius en les energies d'adsorció calculades a causa de les EMSI per a diversos reactius i intermediaris.

En segon lloc, s'investiguen les propietats estructurals i electròniques de la interfície entre una monocapa de FeO 2D i la superfície $\text{CeO}_2(111)$. Les simulacions mostren una geometria interfacial ondulada, consistent amb les observacions experimentals de nanoestructures periòdiques. L'anàlisi de l'estructura electrònica indica la presència de múltiples estats electrònics, assenyalant una interacció complexa entre els parells redox $\text{Fe}^{2+}/\text{Fe}^{3+}$ - $\text{Ce}^{4+}/\text{Ce}^{3+}$. Aquests càlculs també revelen la importància de les interaccions de dispersió i de l'adsorció d'oxigen en l'estabilització de nanoestructures 2D periòdiques de FeO_x .

Finalment, s'estudia la reactivitat química d'un clúster oxidat Pt_6O_9 suportat sobre CeO_2 per copsar l'elevada activitat catalítica de partícules de Pt oxidat suportades sobre cèria en la

reacció d'oxidació de CO per sota de la temperatura ambient. Les energies d'activació de l'oxidació de CO sobre el clúster Pt_6O_9 suggereixen que tant el clúster oxidat com l' O_2 en fase gasosa són les principals fonts d'àtoms d'oxigen per a la formació de CO_2 . Es proposa un mecanisme per a la reacció sobre el clúster Pt_6O_9 on el suport de CeO_2 actua com a espectador dels cicles catalítics descrits. Simulacions cinètiques de Monte Carlo mostren que el mecanisme proposat és consistent amb l'alta activitat catalítica dels clústers d'òxid de Pt per sota de la temperatura ambient.

Paraules clau

Catàlisi heterogènia; Òxid de ceri; Teoria del funcional de la densitat; Interaccions Metall-Suport

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List of Abbreviations

DFT	Density Functional Theory
DOS	Density of States
EMSI	Electronic Metal Support Interactions
EOSI	Electronic Oxide Support Interactions
FRM	First Reaction Method
GGA	Generalized Gradient Approximation
kMC	Kinetic Monte Carlo
KS	Kohn-Sham Orbitals
LDA	Local Density Approximation
LEED	Low Energy Electron Diffraction
MSI	Metal Support Interactions
MvK	Mars-van Krevelen mechanism
PAW	Projector Augmented Wave method
pDOS	Projected Density of States
PW91	Perdew-Wang 91 Functional
RDS	Rate Determining Step
SMSI	Strong Metal Support Interactions
STM	Scanning Tunneling Microscopy
TS	Transition State
TST	Transition State Theory
VASP	Vienna Ab-initio Simulation Package
XPS	X-ray Photoelectron Spectroscopy

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Chapter 1: Introduction

A chemical reaction is “*a process that results in the interconversion of chemical species*”.¹ In this transformation, reactants are transformed into products by a rearrangement of the reactants’ atoms to form new chemical bonds. The change in the concentration of reactants and products as a function of time is known as the reaction rate. The rate v can be influenced by factors such as temperature and concentration of the reactants, as expressed in the general rate equation:

$$v = k[A]^{\alpha}[B]^{\beta} \quad (1.1)$$

where k is the rate constant (which is independent of the concentration and depends on temperature), $[A]$ and $[B]$ are the concentration of the reactants, and α , β are constant exponents corresponding to the partial reaction orders with respect to A and B.

An increase in the reaction rate can be achieved by increasing temperature or changes in the concentration of reactants (depending on the reaction order). A catalyst, as defined by IUPAC, is “*A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction. The catalyst is both a reactant and product of the reaction*”.¹ From this definition, it can be inferred that the role of a catalyst is to modify how a reaction happens (reaction mechanism) to decrease the activation energy and increase the reaction rate (Figure 1.1). Once reactants have been transformed into products, the catalyst is regenerated and available for taking part in a new reaction cycle.

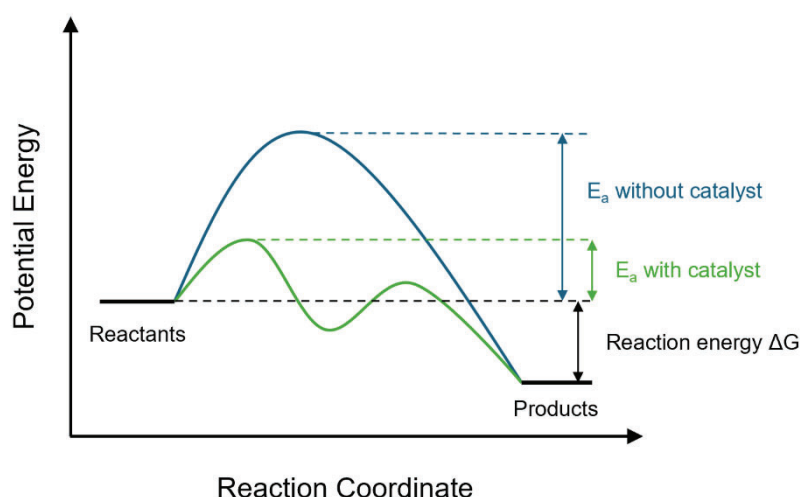


Figure 1.1: Energy profile of a chemical reaction comparing activation energies (E_a) with and without catalyst, illustrating its effect in the reaction mechanism.

Catalysis (“*The action of a catalyst*”)¹ can be classified depending on the nature of the substance that acts as a catalyst. In homogeneous catalysis, the catalyst is in the same phase as the reactants, and in heterogeneous catalysis, the catalyst is in a different phase, e.g. the surface of a solid as a catalyst and reactants in gas-phase.²

1.1 Heterogeneous catalysis

The beginning of heterogeneous catalysis is closely related to industrial processes for the production of organic (mainly derived from coal) and inorganic (mostly sulfur and chlorine compounds) chemicals.³ One of the most notable industrial process based on heterogeneous catalysis is the Haber-Bosch process for the production of ammonia from nitrogen and hydrogen, using an iron-based solid catalyst.⁴ Nowadays, heterogeneous catalysis is involved in around 90% of the production of commercial chemical products.⁵ Catalytic action typically occurs on a material’s surface, with which reactants interact and are transformed into products. Therefore, characterizing the interaction between a material’s surface and reactants, intermediates and products is essential to understand the role of the catalyst in a particular reaction.

When a reactant interacts with a surface, the interaction can be physical (physisorption) or chemical (chemisorption) in nature. Physisorption is a weak interaction based on the polarization of the adsorbate and the surface, while chemisorption involves the formation of a chemical bond between the adsorbate and the surface.² Both interactions can be classified in a broad term called adsorption.⁶ Chemisorption depends strongly on the nature of the adsorption

site, where different adsorption sites are available in a surface. Although there are many types of adsorption sites, the sites that promote catalytic activity are called active sites.

If the interaction of a reactant with the active site of a solid catalyst is too strong, the active sites in the catalyst will not regenerate and deplete over time (this is known as poisoning of the catalyst).⁷ If the strength of the adsorption is too weak, adsorbates will desorb or diffuse (i.e., migrate to a different adsorption site) from the active site too quickly for a reaction to take place. The Sabatier principle⁸ expresses that the optimum performance of a catalyst is achieved when the interaction between the adsorbate and the active site is of an intermediate strength such that poisoning is avoided and dissociation or diffusion are slower than the catalytic reaction.

Another relevant aspect for heterogeneous catalytic reactions is the nature of the solid catalyst. Transition metals (TM) are known to catalyze diverse types of surface reactions such as hydrogenation,⁹ dehydrogenation,¹⁰ Fischer–Tropsch Synthesis,¹¹ among many others. Metal oxides are also commonly used as solid catalysts¹² for reactions like selective oxidation of hydrocarbons,¹³ oxygen evolution,¹⁴ hydrogen evolution reactions,¹⁵ etc.

To improve the performance of a solid catalyst, it is necessary to increase the number of active sites or modify their chemical properties to enable new reaction mechanisms. This can be achieved by nanostructuring active components (increasing surface to volume ratios).^{16–18} Another common strategy is the combination of metals and metal oxides to promote the formation of new active sites, often resulting in very complex structures such as doped surfaces, solid solutions, or supported metal particles of different composition and structural arrangements.¹⁹ Many of these structures are composed of up to millions of atoms, with ideal sizes typically in the nanometer scale.

1.2 Nanostructured catalysts

Different nanostructures can be used as catalysts. Metallic nanoparticles²⁰ are a prime example because of their increased surface to volume ratio and their higher proportion of undercoordinated edge and corner sites, which may have higher activity.²¹ To stabilize nanoparticles and prevent their agglomeration, they are deposited on the surface of another material, which then becomes a support. The support can also influence the chemical properties of the nanoparticles, and the particle-support interface can even participate in chemical reactions. The new properties that emerge from this interaction have been labeled as Metal-Support Interactions (MSI).^{22,23}

MSI depend on the chemical nature of both the nanoparticles and the support, with metallic nanoparticles supported on metal oxides being more frequently studied, although oxide particles supported on metal surfaces (known as inverse catalysts) have also been investigated.²⁴ The interaction of nanoparticles with the support influences their structure and size and can give rise to electronic perturbations such as electron transfer. Solid nanostructured catalysts are usually quite disordered systems with particles of different sizes and shapes. This makes them hard to characterize and precludes establishing reliable relationships between their structure and chemical properties. This is especially relevant at the metal-support interface, since the interaction between the particles, support, reactants and intermediates at the atomic scale will define the catalytic activity of these systems.

The properties of oxide supports are also relevant in defining the chemical properties not only at the metal-support interface but also of the metal nanoparticle as a whole. They can participate in chemical reactions via reactive surface oxygen atoms (reducible oxide) through vacancy formation²⁵ or as non-innocent non-reducible supports.²⁶ If the oxidation state of surface metal atoms in the oxide can change²⁷ due to the interaction with adsorbates or the supported metal nanoparticle, new active sites will be generated, and the mechanistic complexity will increase. For these reasons, cerium oxide (CeO_2) has emerged as a relevant support material for not only metallic nanoparticles, but also oxide particles and nanostructures of higher dimensionality.²⁸

1.3 Cerium oxide and catalytic applications

Cerium (Ce) is a lanthanide with an electronic configuration of $[\text{Xe}] 6s^2 5d^1 4f^1$. Its most common oxidation states are +3 and +4, where the '+4' oxidation state has a noble gas electronic configuration, and '+3' oxidation state exhibits a localized electron in a $4f$ orbital. Interestingly, Ce is as abundant as copper in earth's crust²⁹ and has different technological applications, such as in fuel cells^{30,31} and antibacterial activity.^{32,33}

As a catalytic material, CeO_2 exhibit properties such as Oxygen Storage Capacity (OSC),^{34,35} which is related to facile formation and healing of O vacancies, and an active $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple.^{36–38} These properties enhance the reactivity of CeO_2 , which participates in relevant industrial chemical reactions such as the Water-Gas Shift (WGS) reaction or as part of Three-Way Catalyst (TWC).^{39–42}

The structural characteristics of CeO_2 surfaces also influence their catalytic activity,⁴³ where the most common exposed terminations are (111), (110) and (100). Their predominance determines the shape of CeO_2 crystals, forming octahedral, rods or cubic nanocrystals,

respectively. Which termination is exposed by CeO₂ nanocrystals also influences the particle size of supported metals and their chemical reactivity towards oxidation reactions.^{44–46}

Metallic nanoparticles supported on CeO₂ can activate surface oxygen atoms to take part in oxidation reactions through Mars-van Krevelen reaction mechanism,⁴⁷ which highlights the importance of the reactivity of the support and the different modification strategies to achieve more effective and efficient catalysts. Metallic nanoparticles can also transfer electrons to CeO₂, changing the nature of active sites in the supported particles.^{48,49}

CeO₂ can also act as a support for oxide nanostructures, either in the form of oxide clusters,^{50,51} monolayers, or thin films.^{52–55} This highlights the diverse and rich chemistry of CeO₂ surfaces, which makes it very difficult to elucidate the origin of catalytic activity of CeO₂-based materials through experimental evidence only.

1.4 Computational simulations and models

Computational simulations have become essential to understand different aspects and uncover the complexity around heterogeneous catalysis at the atomic level.⁵⁶ The increase in computational power in the last years⁵⁷ has made simulations of increasingly complex systems composed of hundreds of atoms a routine task. Such computational capacity has made feasible the study of the properties of matter on increasingly larger time and length scales.⁵⁸

In the case of heterogeneous catalysts, aspects such as catalyst structure, environmental effects, mechanistic complexity, and how these aspects relate to each other have become accessible for inquiry by means of experimental model catalysts. A model catalyst is a simplification of a real catalyst that keeps its most relevant structural features without significantly affecting its activity and facilitating the characterization of active sites.^{58–60} The reduced complexity of such experimental model catalysts is also easier to address with representative computational models than the typically more disordered industrial catalysts.

Among the different simulation techniques available, quantum mechanical calculations based on the Density Functional Theory have been the most successful in obtaining atomic-level insights on the catalytic activity of solid surfaces.⁶¹ The computational description of more complex nanostructures is still challenging, but represents a step forward in the understanding and rational design of new solid catalysts.

1.5 Objectives and outline of the thesis

The main objective of this thesis is to use computational modeling based on Density Functional Theory to explore different types of nanostructured catalysts supported on CeO₂ and characterize their electronic, structural, and chemical properties. To address this objective, the following nanostructures are considered:

- A metallic Pt cluster, for which there are gaps in the understanding of the effect of electron transfer to the oxide support on the stability and chemical properties of the system. A more efficient computational methodology is required to enable the systematic study of such electronic metal support interactions to address its effects on the adsorption sites of Pt clusters.
- A 2D FeO_x thin film, to rationalize experimental observations about the structural and electronic properties of the resulting oxide-oxide interface. Experimental evidence suggests a complex structural arrangement and redox behavior as result of the interaction with CeO₂, although the structure of the interface and the extent to which the Fe²⁺/Fe³⁺ and Ce⁴⁺/Ce³⁺ redox couples can stabilize this system is unclear.
- An oxidized PtO_x cluster, to explore its catalytic properties for CO oxidation reaction at temperatures as low as -40°C. Currently, there is not a convincing mechanistic explanation supporting the experimentally measured activity at such low temperatures and the role of the reducibility of CeO₂ is unclear.

Although the proposed nanostructures explore different structural configurations, their choice is motivated by the impact that the reducibility of CeO₂ can have on their electronic and chemical properties and the general relevance of the CeO₂ support in heterogeneous catalysis.

The present thesis is structured as follows:

Chapter 2 briefly describes the theoretical background and the computational methods used throughout this thesis.

Chapter 3 proposes a computational protocol for systematically addressing Electronic Metal Support Interactions on cerium oxide-based materials, using as a test system a supported Pt cluster. The effects of the interaction with the support on the chemical reactivity of the Pt cluster are explored under the suggested computational strategy.

Chapter 4 describes an experimental-computational collaboration to study the modification of cerium oxide with iron. In particular, a crystalline FeO_x/CeO₂ oxide-oxide interface is

identified, and its structural and electronic properties are elucidated with computational modeling.

Chapter 5 evaluates the reactivity of ceria-supported PtO_x clusters for CO oxidation at temperatures below 0°C. A reaction mechanism is proposed and kinetic Monte Carlo simulations are used to explore the catalytic activity of these clusters at different temperatures.

In Chapter 6, the main conclusions of this thesis are reported.

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Chapter 2: Theoretical background and methodology

2.1 The Schrödinger equation

The main objective of quantum chemistry is to describe the behavior of electrons in atomic and molecular systems. The approach is based on solving the Schrödinger equation:¹

$$\hat{H}\Psi = \varepsilon\Psi \quad (2.1)$$

This is an eigenvalue equation where $\hat{H}$ is the Hamiltonian operator, Ψ is the wave function which represents the electrons and nuclei of an atomic or molecular system and ε is the energy associated with the Hamiltonian operator applied to this wave function. The Hamiltonian operator describes the energy of a system by the following equation:

$$\hat{H} = -\sum_{i=1}^n \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2m_A} \nabla_A^2 - \sum_{i=1}^n \sum_{A=1}^M \frac{Z_A}{|R_A - r_i|} + \sum_{i=1}^{n-1} \sum_{j>i}^N \frac{1}{|r_i - r_j|} + \sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{|R_A - R_B|} \quad (2.2)$$

where the first and second terms are the kinetic energy of electrons and nuclei, respectively; the third term is the electron-nucleus attraction and the fourth and fifth term are the electron-electron and nucleus-nucleus repulsion, respectively.

Given that nuclei are much heavier than electrons in terms of mass, it is assumed that electrons move in a field of fixed nuclei. This assumption is called the Born-Oppenheimer approximation² and reduces the Hamiltonian operator to an electronic Hamiltonian where the kinetic energy of nuclei is 0 and the nucleus-nucleus interaction is constant with the form:

$$\hat{H}_{el} = -\sum_{i=1}^n \frac{1}{2} \nabla_i^2 - \sum_{i=1}^n \sum_{A=1}^M \frac{Z_A}{|R_A - r_i|} + \sum_{i=1}^{n-1} \sum_{j>i}^n \frac{1}{|r_i - r_j|} \quad (2.3)$$

The system to which the Hamiltonian operator is applied is described by the wave function:

$$\Psi(x_1, x_2, \dots, x_n) \quad (2.4)$$

Where x_n represents the spatial and spin coordinates of each electron in the system. But for the wave function to have a physical interpretation, the product of the wave function and its complex conjugate of it must be taken:

$$\Psi^*(x)\Psi(x) = |\Psi(x)|^2 \quad (2.5)$$

as this corresponds to the probability density function.

There are certain mathematical properties that the wave function must satisfy to be a good representation for electrons in an atomic or molecular system. First, since electrons are indistinguishable from each other, any change in the coordinates of 2 electrons will not change the probability of finding those electrons in the same space:

$$|\Psi(x_1, x_2, \dots, x_i, x_j, \dots, x_n)|^2 = |\Psi(x_1, x_2, \dots, x_j, x_i, \dots, x_n)|^2 \quad (2.6)$$

Second, the fact that electrons are fermions which have spin values that are half integers (1/2 and -1/2) means the wave function should be antisymmetric with respect to the change in coordinates of 2 electrons in the system:

$$\Psi(x_1, x_2, \dots, x_i, x_j, \dots, x_n) = -\Psi(x_1, x_2, \dots, x_j, x_i, \dots, x_n) \quad (2.7)$$

Which is the generalization of Pauli's exclusion principle which states that 2 electrons cannot occupy the same state.

Lastly, given the probabilistic interpretation of the wave function, as shown in eq. 2.5, the integration over the space defined by the spatial coordinates of the electrons should be unity.

$$\int \int \dots \int |\Psi(x_1, x_2, \dots, x_n)|^2 dx_1 dx_2 \dots dx_n = 1 \quad (2.8)$$

If the wave function satisfies this requirement, it's said to be normalized.

Wave function methods are based on the use of spin orbitals as representations of the wave function. Spin orbitals have a spatial part (spatial orbital) and a spin component, where for a single spatial orbital, two spin orbitals can be obtained:³

$$\chi(x) = \psi(r)\alpha(\omega) \text{ or } \psi(r)\beta(\omega) \quad (2.9)$$

where $\psi(r)$ is the spatial part and $[\alpha(\omega) \text{ or } \beta(\omega)]$ is the spin part of the wave function.

For the spin orbitals to satisfy the Pauli principle, the wave function for the whole system can be written as a Slater determinant of spin orbitals:⁴

$$\Psi(x_1, x_2, \dots, x_n) = (n!)^{-1/2} \begin{vmatrix} \chi_1(x_1) & \dots & \chi_n(x_1) \\ \vdots & \ddots & \vdots \\ \chi_1(x_n) & \dots & \chi_n(x_n) \end{vmatrix} \quad (2.10)$$

Where n represents the number of electrons in the system, $(n!)^{-1/2}$ is a normalization factor related to the orthogonal nature of the spin orbitals.

Although they offer high accuracy, wave function methods become extremely expensive for large numbers of electrons. However, there is another approach for calculating the electronic structure based on the electron density called “Density Functional Theory”.

2.2 Density Functional Theory

Density Functional Theory (DFT)⁵ is a methodology which uses as a central quantity the electron density. The electron density can be written as follows:

$$\rho(\mathbf{r}) = N \int \dots \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (2.11)$$

which expresses the probability of finding an electron in a given volume element. This quantity must vanish when the distance goes to infinity and the result of integrating it must be the total number of electrons of the described system.

If the objective is to describe the properties of a system composed of electrons moving around fixed nuclei (following the Born-Oppenheimer approximation) solving the Schrödinger equation, using the electron density requires it to fulfill some conditions which are known as the Hohenberg-Kohn theorems.⁶

2.2.1 Hohenberg-Kohn Theorems

Two theorems demonstrate that the electron density satisfy the requirements to solve the Schrödinger equation. The first theorem states: “*The external potential $V_{ext}(\mathbf{r})$ of a non-degenerate electronic state is a unique functional of the electron density $\rho(\mathbf{r})$* ”. This theorem proves that from an external potential, the total energy of the system can be calculated as:

$$E[\rho] = \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + F_{HK}[\rho] \quad (2.12)$$

The term $F_{HK}[\rho]$ is known as the universal functional, independent of the number of electrons and nuclear coordinates.

The second theorem states: “*For a given density $\rho(\mathbf{r})$, if this density minimizes the energy, then the ground state energy can be obtained variationally*”. This can be expressed simply as:

$$E_0 \leq E[\rho(\mathbf{r})] \quad (2.13)$$

Although this is another expression of the variational principle which is central for wave function methods, both theorems allow us to replace the $3N$ dimensions of the wave function with the electronic density that depends only on three spatial coordinates.

2.2.2 Modern implementation of DFT: Kohn-Sham equations

Under the formalism provided by the Hohenberg-Kohn theorems, Kohn and Sham provided a method to compute the energy of any given system.⁷ Their proposal was to replace the real system with a system of N non-interacting particles under an effective potential $V_{KS}(\mathbf{r})$ that matches the original density $\rho(\mathbf{r})$. Then the total electron density can be expressed as:

$$\rho_{KS}(\mathbf{r}) = \sum_{i=1}^N |\phi_i^{KS}(\mathbf{r})|^2 \quad (2.14)$$

Where the term $\phi_i^{KS}(\mathbf{r})$ is a one electron orbital labeled as the Kohn-Sham (KS) orbital. Having calculated the electron density from the KS orbitals, the energy of the system can now be expressed as:

$$E_{KS}[\rho] = \sum_i^N \varepsilon_i^{KS} = T_{KS}[\rho] + \int \rho(\mathbf{r}) V_{KS}(\mathbf{r}) d\mathbf{r} \quad (2.15)$$

Here, the term $T_{KS}[\rho]$ is the Kohn-Sham kinetic energy of the electrons in the non-interacting system and the effective potential $V_{KS}(\mathbf{r})$ can be considered as follows:

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{ee}(\mathbf{r}) + V_{xc}(\mathbf{r}) \quad (2.16)$$

where $V_{ext}(\mathbf{r})$ is the external potential, $V_{ee}(\mathbf{r})$ is the Coulombic repulsion between electrons and $V_{xc}(\mathbf{r})$ is the exchange-correlation potential. The exchange-correlation potential is the functional derivative of the exchange-correlation functional $E_{xc}[\rho]$ and represents the energy difference between the non-interacting system and the real many-body system. The exact expression of the $E_{xc}[\rho]$ is unknown and must be approximated for calculating the total energy of a system.

2.2.3 Exchange-correlation functionals

In order to perform a DFT calculation, an approximate $E_{xc}[\rho]$ must be used. Several functionals have been proposed over the years with increasing complexity and computational cost. These

functionals have been classified in Jacob's Ladder,⁸ which showcases different levels of sophistication with the last step in the ladder being the exact form of the exchange-correlation functional. The first and simplest approximation to the $E_{xc}[\rho]$ is the Local Density Approximation (LDA),⁹ which depends only on the electron density and describes it as a homogeneous electron gas.

$$E_{xc}^{LDA} = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho) d\mathbf{r} \quad (2.17)$$

This family of functionals have good performance for bulk metals which have homogeneous electronic distributions, but for atoms and molecules its accuracy is rather poor.

The next step is the Generalized Gradient Approximation (GGA) functionals,¹⁰ where the gradient of the density ($\nabla\rho(\mathbf{r})$) is included explicitly.

$$E_{xc}^{GGA} = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) d\mathbf{r} \quad (2.18)$$

The inclusion of $\nabla\rho(\mathbf{r})$ allows an appropriate description of variations in the electron density for smaller systems such as atoms or molecules. Further improvements on $E_{xc}[\rho]$ come from including the Laplacian of the density in what are known as meta-GGA functionals or including part of non-local exchange from HF into the $E_{xc}[\rho]$ forming the hybrid functionals.

In this thesis, only the GGA functional Perdew-Wang 91 (PW91)¹¹ is used for all calculations. PW91 offers a good compromise between accuracy and computational cost for systems with large numbers of atoms.^{12,13}

2.2.4 Extended systems

To perform a DFT calculation and correctly describe the electron density, basis functions are needed. For atomic and molecular systems, localized basis functions such as Gaussian-type orbitals (GTO) or Slater-type orbitals (STO) are used.^{3,14} However, systems with periodic structures such as solids need to be described by other types of basis functions such as plane waves.

$$PW(\vec{k}, \vec{r}) = e^{i\vec{k}\vec{r}} \quad (2.19)$$

where k is a wave vector. Plane waves are not centered around atoms but are distributed across space which makes them very convenient to evaluate periodic systems. However, large numbers of plane waves are required to describe all electrons in atoms, especially those in core regions. To address this issue, the Projector Augmented Wave (PAW)¹⁵ method is used. This method treats core electrons as fixed electrons using pseudopotentials and explicitly evaluating only valence electrons that are relevant for chemical processes such as bonding.

For this thesis, the PAW method as implemented in the Vienna Ab-initio Simulation Package (VASP)^{16–18} is used for all calculations. The energy convergence threshold for the self-consistent field calculation is 5×10^{-6} eV and for geometry optimizations, atoms are allowed to displace until the forces acting upon them are smaller than $0.05 \text{ eV } \text{\AA}^{-1}$.

2.2.5 On-site Coulomb interactions: DFT+U

In DFT calculations using approximations to the $E_{xc}[\rho]$ such as GGA functionals, there is an incomplete cancelation of the unphysical interaction between an electron and the electron distribution to which that same electron belongs. This is called the self-interaction error (SIE) and in the case of strongly correlated systems with electrons localized on d or f orbitals, it can lead to wrong half-occupancies of these orbitals. An effective approach to deal with SIE and obtain a correct physical localization of these electrons is to introduce an additional term to the total energy, through a semi-empirical parameter U_{eff} which specifies the strength of the on-site Coulomb interaction:

$$E_{DFT+U} = E_{DFT} + \frac{U_{eff}}{2} \sum_{\sigma} \left[\left(\sum_m \rho_{m,m}^{\sigma} \right) - \left(\sum_{m,n} \rho_{m,n}^{\sigma} \rho_{n,m}^{\sigma} \right) \right] \quad (2.20)$$

where $\rho_{m,m}^{\sigma}$ is the density matrix of the orbitals to which the correction is applied. The result of this correction is an energy penalty for half-occupied states, making either a fully occupied state or an unoccupied state lower in energy (i.e. more stable).

In this thesis, U_{eff} values of 4 eV for $4f$ electrons of Ce and 5 eV for $3d$ electrons of Fe are used, as described in references 19 and 20, respectively. The implementation of this correction in VASP corresponds to the approach proposed by Dudarev et. al.²¹

2.2.6 Dispersion corrections

Another limitation of DFT is the lack of description of dispersion or Van der Waals (VdW) forces. These arise from fluctuations of the electron density that originates instantaneous

dipole-dipole interactions. Dispersion forces are long-range forces, in distances from atomic nuclei where the electron density is smaller. To account for these forces, a straightforward solution is provided by including a semi-empirical term to the total DFT energy:²²

$$E_{tot} = E_{DFT} + E_{disp} \quad (2.21)$$

The dispersion energy term is given by:

$$E_{disp} = -s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{C_6^{ij}}{R_{ij}^6} f_{damp}(R_{ij}) \quad (2.22)$$

where s_6 is a scaling factor that depends on the density functional chosen, C_6^{ij} is the dispersion coefficient for the atom pair ij and R_{ij} is the interatomic distance between atoms ij . The f_{damp} term is a damping function to avoid errors for small R_{ij} values.

For this thesis, Grimme's D2 correction²³ was used for the PW91 functional where C_6 and R_0 values for Ce are 20.0 (J·nm⁶/mol) and 1.860 Å,^{24,25} for Fe are 10.8 (J·nm⁶/mol) and 1.562 Å²³ and for O atoms, the values are 0.7 (J·nm⁶/mol) and 1.342 Å.²³

2.3 Transition State Theory

The first assessment of the rate of a chemical reaction was done by Arrhenius²⁶ in 1889 to explain the temperature dependence of reaction rates:

$$k = Ae^{\frac{-E_a}{RT}} \quad (2.23)$$

where A is a pre-exponential factor, E_a is the activation energy of the reaction, R is the gas constant and T is the temperature in Kelvin.

Later, Transition State Theory^{27,28} postulates the existence of an intermediate structure between reactants and products, called the transition state (TS). In this theory, reactants and products are located at local minima points of a Potential Energy Surface (PES), which correlates the energy of chemical species with their coordinates in space.²⁹ In a chemical reaction there is a change in the structure of reactants that requires a displacement through the PES from one local minima point to the other. The displacement of the atoms of the reactants will generate an intermediate structure, the TS. This TS is considered a saddle point in the PES because it minimizes the forces acting upon the atoms, while being a local maximum of the energy.

The energy difference between the reactants and the TS is the activation energy and is related to the reaction rate by the following equation:

$$k_{TST} = \frac{k_B T}{h} \frac{q_{TS}^\ddagger}{q_r} e^{\frac{-\Delta E_a}{k_B T}} \quad (2.24)$$

where k_B is Boltzmann's constant, h is Planck's constant and with $q_{TS}^\ddagger$ and q_r being the partition function of the TS and the reactants, respectively.

For the calculation of transition states, the Nudged Elastic Band (NEB)³⁰ method is used. This method optimizes a certain number of intermediate structures (images) between reactants and products. The optimization of the images considers the total force acting on the image as a sum of a spring force along the reaction coordinate and the force perpendicular to the reaction coordinate. The structure of a TS is the one where the forces along the reaction coordinate are zero. An improvement of the NEB method is the Climbing Image Nudged Elastic Band (CI-NEB),³¹ where the forces on the image with the highest energy are calculated only perpendicular to the reaction coordinate without considering forces along the reaction coordinate.

In this thesis, the NEB and CI-NEB methods are used to calculate transition states, where the CI-NEB method is applied to refine reaction coordinates calculated initially with the NEB method.

2.4 Kinetic Monte Carlo simulations

Electronic structure calculations have become an indispensable tool for rationalizing catalytic activity and reaction kinetics, where they can be used to understand the average kinetic properties of a catalyst based on the coverage by adsorbates. This requires a catalyst with uniform active sites, but real catalysts have different types of active sites which necessitate a more detailed description.

Kinetic Monte Carlo (kMC)³² is a set of simulation techniques for reaction kinetics where reactive events are defined, and their occurrences are randomly generated. In kMC simulations, a system consists of a set of active sites where reactive events take place and the main objective is to solve the chemical master equation:

$$\frac{dP_\alpha}{dt} = \sum_\beta W_{\alpha\beta} P_\beta - W_{\beta\alpha} P_\alpha$$

(2.25)

where P_α is the probability to find the system in the state α and $W_{\alpha\beta}$ corresponds to the transition rate from state β to α , as given in eq. 2.24. The states can be defined as the specific occupation of a given site.

There are several methods to perform a kMC simulation. One of them is the First Reaction Method (FRM) which consists on chronologically executed reactive events based on a random uniform time of occurrence:

$$t_{\beta\alpha} = t - \frac{\ln(u)}{W_{\beta\alpha}} \quad (2.26)$$

For a process $\alpha \rightarrow \beta$, $t_{\beta\alpha}$ is the time when the event takes place, t is the initial time, $W_{\beta\alpha}$ is the rate constant for the process and u is a random uniform value in the interval from 0 to 1.

In this thesis, kMC simulations are performed using the FRM as implemented in the MonteCoffee application developed by Jørgensen and Grönbeck.³³

2.5 References

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Chapter 3: Electronic Metal-Support Interactions: Pt/CeO₂ case systems.

3.1 Introduction

Metal-Support Interactions (MSI) induce significant changes in the electronic and geometrical properties of supported metals.¹⁻³ These changes can notably affect the catalytic performance of the latter. The first type of MSI to be identified was Strong Metal-Support Interactions (SMSI) inhibiting the chemisorption of molecules on noble metals supported on TiO₂ resulted from the encapsulation by the oxide.⁴

EMSI (Electronic Metal Support Interactions) are a particular type of MSI referred to a electron transfer processes taking place between a metal particle and a reducible support. This effect was first identified for Pt clusters supported on CeO₂,⁵ and since then this behavior has been observed for different metals and reducible oxides.⁶⁻¹⁰

EMSI opens new possibilities for tuning reactivity through changes on the oxidation state of metal atoms at the interface with the support.¹¹ Different charge states of supported metal particles can be exploited to modify their chemical reactivity and thus promote new catalytic processes of fundamental and applied importance.^{12,13}

Important factor for the evaluation of the EMSI effects on the chemical reactivity at metal-oxide interfaces is the characterization of the different charge states of the supported metallic species.¹⁴⁻¹⁶ These states are described by the total number of electrons that a metal particle can donate to the reducible oxide (or receive from the latter).¹⁷ Such electron donation often results in a high number of possible electronic states defined by the number of reduced atoms in the oxide support and positions of the reduced atoms with respect to the metal particle.^{18,19}

The stability of different electronic states and the effect of changes in the oxidation states of metal particles and reducible supports are not well understood. Factors such as particle size, chemical evolution of supported particles due to oxidative or reductive reaction conditions may hinder the extent up to which EMSI can influence the catalytic activity at the metal-oxide interface.²⁰⁻²⁴

Computational simulations allow a detailed exploration of the multitude of electronic states of supported metal particles and predicting the influence of various states on the chemical reactivity of the metal-oxide interface.²⁵ However, a systematic approach to EMSI is lacking

due to numerous electronic states involved, difficulties with the accurate description of highly correlated materials (for instance, CeO_2), and designing representative structural models of supported metal particles.

This chapter outlines a computational methodology for a systematic characterization of the EMSI in CeO_2 -based materials. In particular, a $\text{Pt}_8/\text{CeO}_2(111)$ model is studied, addressing its different electronic states by explicitly considering the electron transfer process, changes in the charge state of the supported Pt_8 cluster and impact of these phenomena on the chemical properties of the metal-oxide interface.

3.2 Computational Models

Pt particles are represented by an 8 atoms platinum cluster supported on a (3×3) $\text{CeO}_2(111)$ surface formed by 3 O-Ce-O tri-layers. The bottom tri-layer of the surface model is kept fixed on bulk positions. (Figure 3.1).

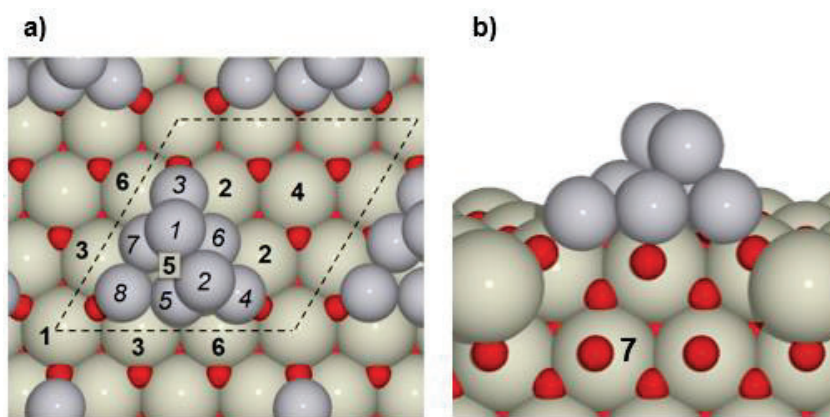


Figure 3.1: Pt_8/CeO_2 model, where a) top view and b) side view. Numbers indicate the labels designated for different Ce atoms in the surface (bold numbers) and Pt atoms of the cluster (italic numbers), respectively. Beige, red and grey spheres represent Ce, O and Pt atoms and the dashed lines outline the 3×3 CeO_2 surface supercell.

The lattice parameter of the $\text{CeO}_2(111)$ support is $5.41 \text{ \AA}$, which is the experimental lattice parameter, and it is compressed by 1.46% with respect to the optimized lattice parameter of $5.49 \text{ \AA}$ obtained for the PW91+U methodology described in Chapter 2.

To describe the changes in the oxidation state of Ce atoms in the support, a special pseudopotential that fixes $4f$ electrons in the core to explicitly define a Ce^{3+} cation is used. This potential is called `Ce_3` (11 May 2000) in the VASP pseudopotential library and for the purpose of this work it will be called `Ce4f-core` potential. In the same venue, the pseudopotential that treats explicitly the $4f$ electron of Ce atoms will be labeled as `Ce4f-valence` potential. The use

of Ce4*f*-core potentials along with local relaxations at the non-spin polarized level results in pre-conditioned structures with the desired number and positions of Ce³⁺ cations that induce structural perturbations in the surface.

Using this previously optimized structure and a proper initial guess for the magnetization of the corresponding Ce³⁺ (± 1), a local relaxation at the spin polarized level with an explicit treatment of 4*f* electrons is carried out. However, this procedure does not ensure the convergence to the desired electronic state.

In a (3×3) supercell, the Pt clusters are separated by ~5.9 Å from their respective periodic images, thus ensuring a good compromise between particle density and computational cost. Another important aspect is that a (3×3) supercell consists of 9 surface Ce atoms, which makes possible a systematic evaluation of different electronic states, considering different numbers and positions of Ce³⁺ around the Pt₈ cluster.

3.3 Results

For the characterization of different electronic states of Pt₈/CeO₂, it is necessary to calculate the total energy of systems with different numbers and positions of Ce³⁺ cations. For that the electronic states accessible for the system are calculated using the Ce4*f*-core potential to describe the present Ce³⁺ cations and the standard Ce4*f*-valence potential to describe the Ce⁴⁺ cations. This approach has the advantage of precisely defining different electronic states. On the other hand, it introduces changes in the basis sets of systems with different numbers of Ce³⁺ cations, which hampers energy comparison of such systems. To overcome this problem, structures obtained with the Ce4*f*-core potential are subsequently optimized using the Ce4*f*-valence potential, treating explicitly 4*f* electrons. Thus, obtained results allow for comparison of electronic states of a given stoichiometry with different numbers of Ce³⁺ cations and the identification of the most stable electronic state. Energies obtained for electronic states calculated with Ce4*f*-core potential can be shifted by the energy differences between the most stable states for each particular number of Ce³⁺, as shown in Figure 3.2

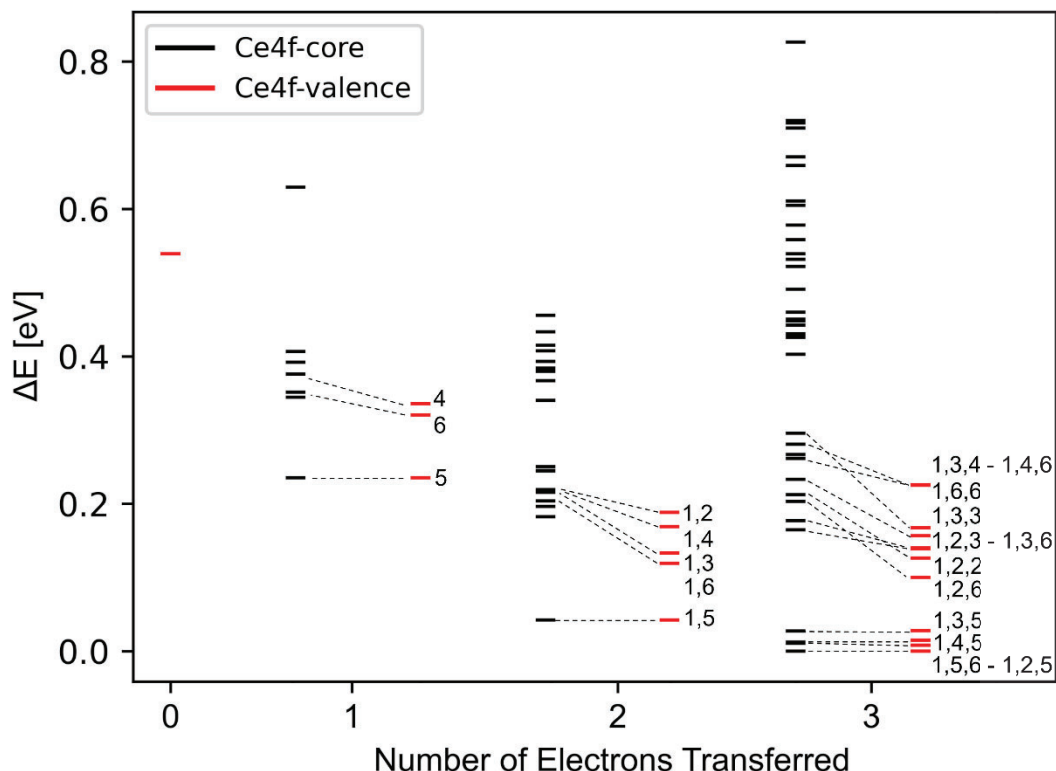


Figure 3.2: Relative energies of electronic states calculated with $Ce4f$ -core (black marks) and $Ce4f$ -valence (red marks) potentials for different numbers and positions of Ce^{3+} cations formed by electron transfer from the Pt_8 cluster to the $CeO_2(111)$ support. Numbers next to the red marks indicate the positions of Ce^{3+} labeled in Figure 3.1 and dashed lines connect the same electronic states calculated combining the $Ce4f$ -core with $Ce4f$ -valence potentials (for the $4f^1$ - Ce^{3+} and $4f^0$ - Ce^{4+} cations, respectively) and solely using the $Ce4f$ -valence potentials for both the Ce^{3+} and Ce^{4+} cations.

$\Delta E(Ce4f\text{-core})$ shows that different electronic states can feature energy differences up to 0.82 eV, depending on the relative positions of Ce^{3+} cations on the surface with respect to the Pt_8 cluster. The most stable electronic state corresponds to 3 transferred electrons to the $CeO_2(111)$ surface; the energy difference with the most stable states for 2, 1 and 0 transferred electrons is 0.03, 0.22 and 0.54 eV, respectively. Also, there are several states with energy differences below 0.1 eV which imply a high mobility of Ce^{3+} cations on the surface.

As can be seen in Figure 3.2, the energy differences between the same electronic states described by $Ce4f$ -core and $Ce4f$ -valence potentials do not match exactly, but a trend of stabilization observed by explicitly accounting for the $4f$ electron is reasonably well reproduced. These energy differences in case of the usage of $Ce4f$ -core potential can be attributed to such factors as absent magnetic coupling of $4f$ electrons, the impossibility of core electrons to participate in bonding (Ce-O bonds) and stronger electrostatic interactions.

Interesting trends have been observed regarding the formation of Ce^{3+} cations. Positions close to the Pt_8 cluster seem to be more favorable for the localization of $4f$ electrons. This may be explained by the interaction between the Pt_8 cluster and the CeO_2 surface, where Pt-O bonds will lead to distorted Ce-O bonds, creating more space around those Ce atoms to accommodate an extra electron. Also, the formation of a Ce^{3+} cation will create distortions in the surface Ce-O bonds, where an O- Ce^{4+} bond is ~ 2.3 to 2.45 Å long, while an O- Ce^{3+} bond is somewhat longer, ~ 2.4 to 2.6 Å. The O- Ce^{3+} bond distances are in very good agreement, when calculated using Ce $4f$ -core and Ce $4f$ -valence potentials to describe Ce^{3+} cations. The close agreement of the bond-lengths obtained by using the two kinds of potentials in describing this key structural parameter further corroborates the strategy to use the Ce $4f$ -core potential to precondition the structure of Pt_8/CeO_2 before describing Ce $4f$ electrons explicitly.

After illustrating the reliability of the Ce $4f$ -core potentials to describe the formation of Ce^{3+} cations in the $\text{CeO}_2(111)$ surface area, the next step is to analyze the effects of EMSI on the electronic structure of the supported Pt_8 cluster. Given the different computational approaches that can be used to explore EMSI, such as Ce $4f$ -core potentials or the consideration of spin polarization, it is important to address the impact of these approaches on the description of the electronic properties of the Pt_8 cluster. The changes in the electronic structure of the Pt_8 cluster upon electron transfer are described by the evolution of its Density of States (DOS) and by a Bader charge analysis.

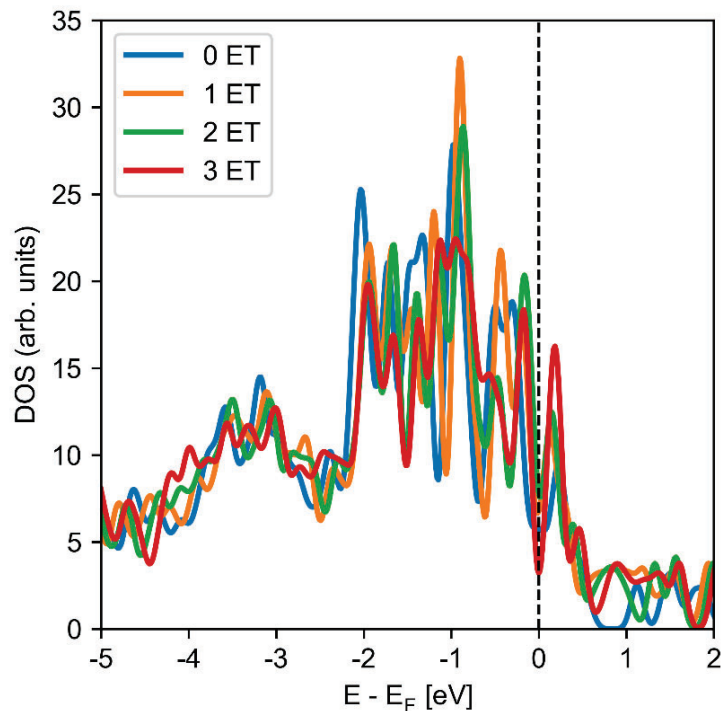


Figure 3.3: Total Density of States of the Pt_8 cluster supported on $\text{CeO}_2(111)$ for the most stable electronic state calculated for a particulate number of Ce^{3+} cations formed: electron transfer (ET) of 0, 1, 2 and 3. Energies are shifted with respect the Fermi levels indicated by the vertical dashed line.

Given the complexity of the electronic structure of the entire Pt_8 cluster for different electronic states (see Figure 3.3), the projected Density of States (pDOS) on specific atoms of the Pt_8 cluster is analyzed comparing the state with no electrons transferred with the most stable state with 3 electrons transferred (Figure 3.4), for a Pt atom at the interface with the CeO_2 support and a Pt atom in the upper layer of the cluster most distant from the support.

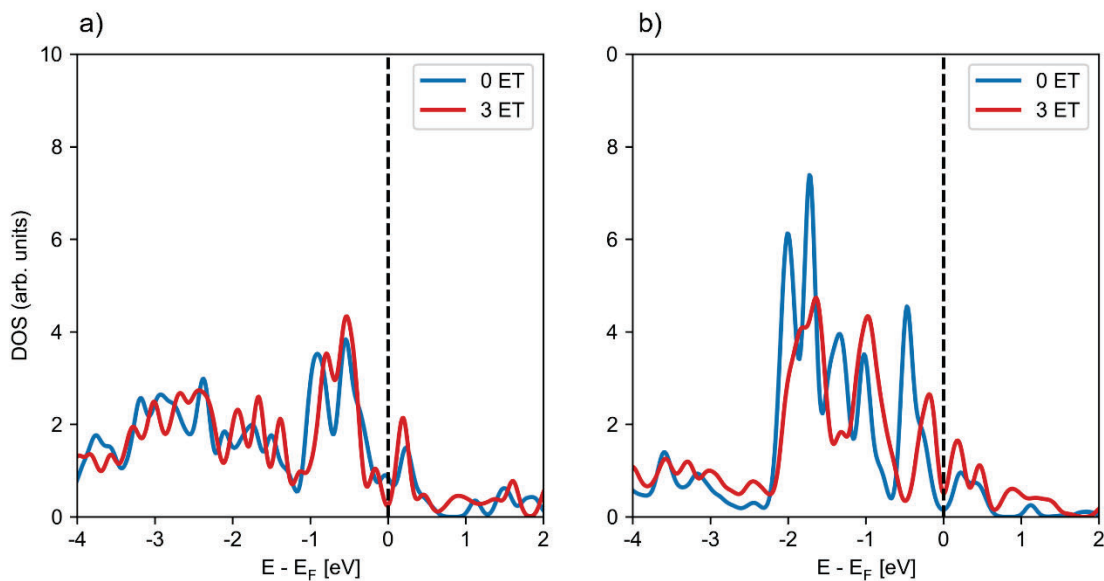


Figure 3.4: Projected Density of States (pDOS) of a) Pt-1 and b) Pt-8 atoms (the numbers are the labels defined in Figure 3.1) for the most stable electronic state obtained (3 electrons transferred) and the electronic state without electrons transferred to the CeO₂ support. The vertical dashed line indicates the Fermi level as reference value for the energy values.

From the pDOS plots, it can be inferred that EMSI noticeably influence interface Pt atoms, while Pt atoms that are not in direct contact with the surface are barely affected. Another result is inhomogeneous charge redistribution upon electron transfer, given the shift in the pDOS peaks for the interface Pt-8 atom.

The inhomogeneous effect of EMSI in the electronic structure of the supported Pt₈ cluster is also described by a Bader charge analysis. The differences in the atomic charges of the Pt₈ cluster calculated for different electronic states show that interface atoms are the most affected by electron transfer (Figure 3.5).

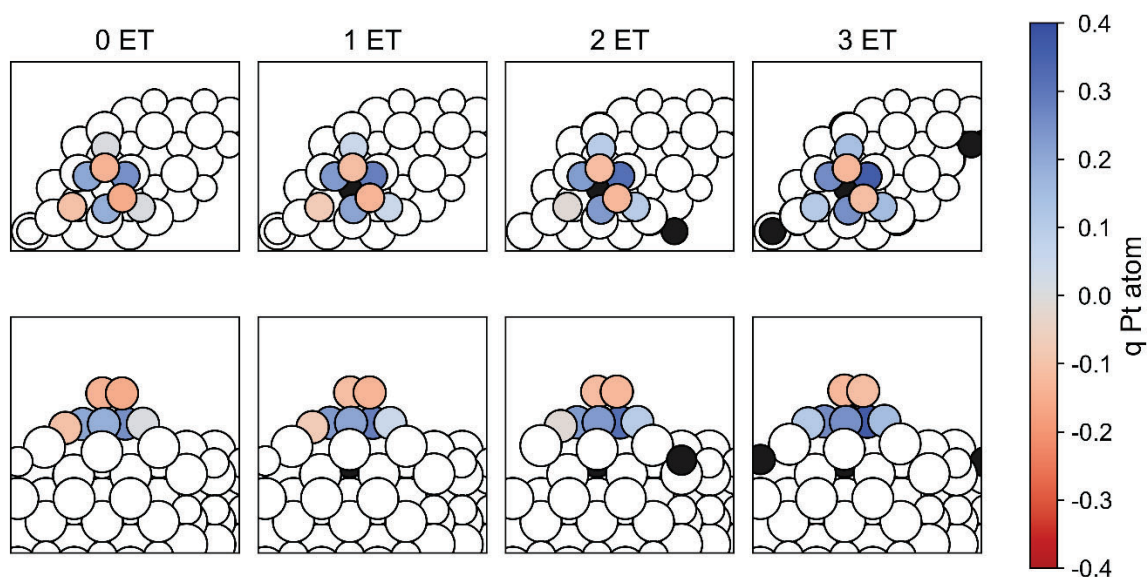


Figure 3.5: Bader charges (q) of atoms of the Pt_8 cluster supported on CeO_2 . The charges are calculated for the most stable electronic state from 0 to 3 electrons transferred (ET), with Pt atoms colored according to their respective charge indicated by the right-hand side color bar: red is negative charge and blue is positive charge. Black circles denote Ce^{3+} cations in the surface.

After exploring the EMSI effects on the electronic structure of Pt_8 clusters, the next step is to evaluate the chemical properties of the clusters and how electron transfer can impact them. From the characteristics evaluated from pDOS and Bader charges, two adsorption sites are defined in the cluster at the interface and in the second (upper) layer, exploiting the features derived from the electronic structure analysis performed. First, it is necessary to assess how suitable $\text{Ce}4f$ -core potentials are for the description of chemical properties of the cluster such as adsorption energies. For this, a CO molecule is used as a probe molecule comparing different adsorption sites and electronic states.

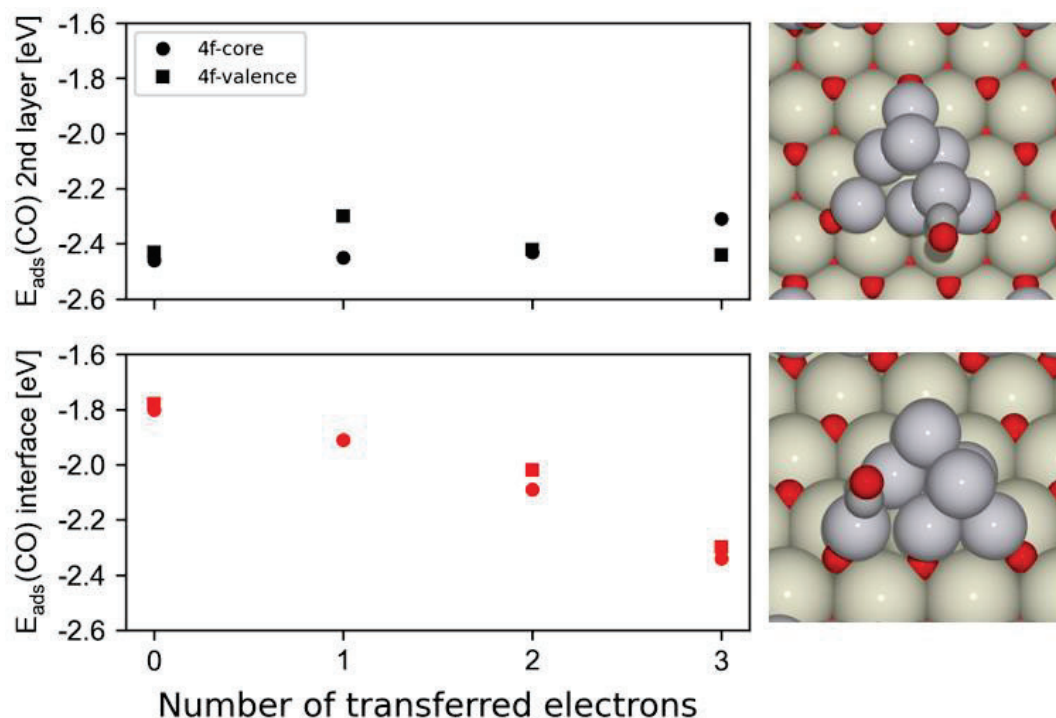


Figure 3.6: CO adsorption on second layer (Pt-1) and interface (Pt-8) atoms of the Pt_8 cluster supported on $\text{CeO}_2(111)$. Adsorption energies are calculated using spin-restricted and $\text{Ce}4f$ -core (circles) approach compared to the corresponding spin-unrestricted and $\text{Ce}4f$ -valence (squares) data. The adsorption geometry is illustrated on the right-hand side panels.

CO adsorption energy is calculated as:

$$E_{\text{ads}} = E(\text{Ads-Pt}_8/\text{CeO}_2) - E(\text{Ads}) - E(\text{Pt}_8/\text{CeO}_2)$$

where $E(\text{Ads-Pt}_8/\text{CeO}_2)$ and $E(\text{Pt}_8/\text{CeO}_2)$ are the total energies of the system with and without the adsorbate, respectively. As seen in Figure 3.6, the $\text{Ce}4f$ -core potential shows quantitative agreement in describing the changes induced in the electronic structure of supported Pt_8 clusters with respect to $\text{Ce}4f$ -valence potential, with the biggest difference in adsorption energy below ~ 0.1 eV and thus reproducing the changes in the chemical properties of Pt_8 sufficiently well.

Beyond CO molecule, the effect of EMSI on the chemical reactivity has been evaluated for three other typical adsorbates and reactants - H atom, H_2O and OH molecules (Figure 3.7).

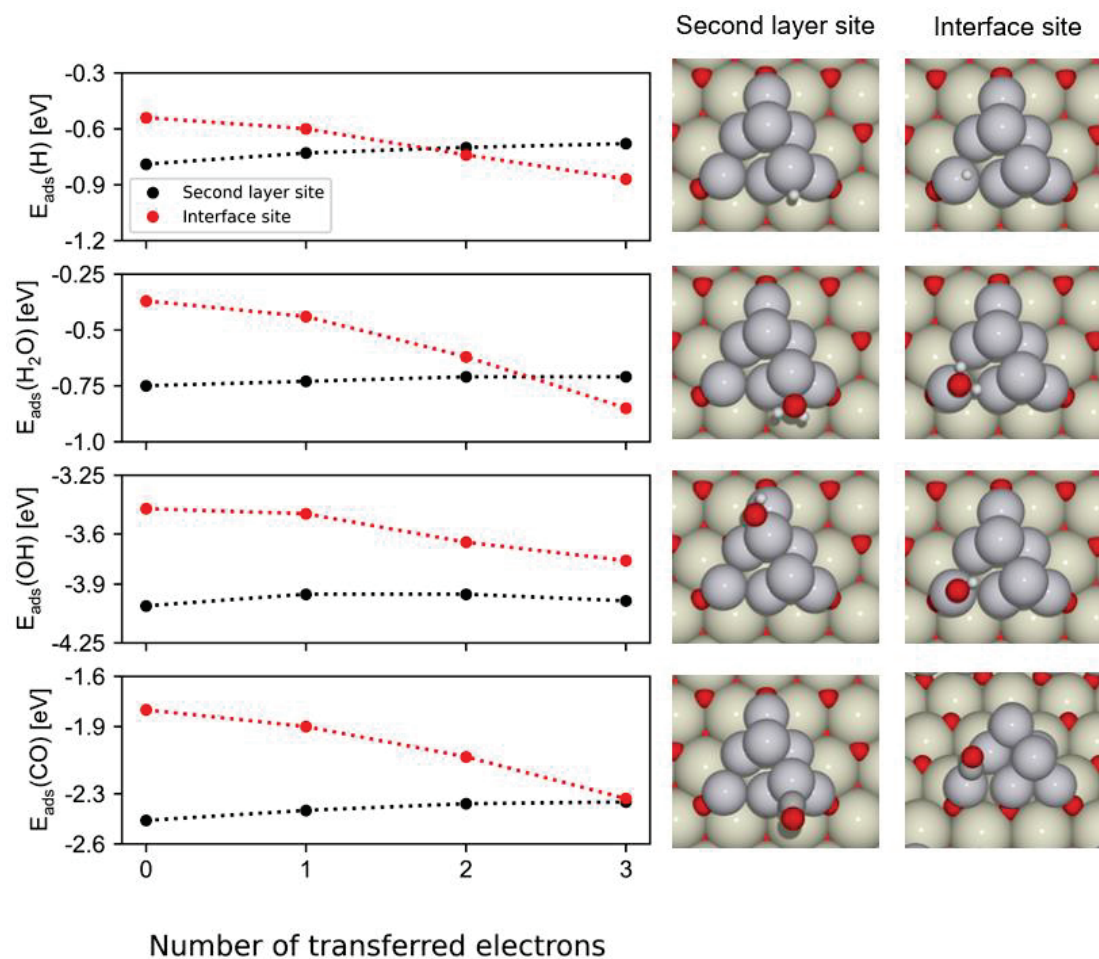


Figure 3.7: Adsorption energy of H, H₂O, OH and CO on Pt₈/CeO₂(111) for the most stable electronic states from 0 to 3 transferred electrons. The black and red markers represent the second (upper) layer adsorption site and the interface adsorption site, respectively. The adsorption sites evaluated are illustrated in the right-hand side panels.

The adsorption energies at the interface site evolve as a consequence of EMSI, where upon electron transfer the interaction of the adsorbates becomes stronger while the second-layer site is much less affected. Given that without electron transfer the second-layer site is a more favorable adsorption site, EMSI can strengthen the adsorption energy on the interface site by up to 0.3-0.5 eV and produce an inversion in the preferred adsorption site. An intriguing aspect of the adsorption energy change is that the EMSI does not alter the bond distances between Pt atoms and the adsorbate. This effect might be attributed to electrostatic interactions between Ce³⁺ centers and interface Pt atoms.

3.4 Conclusions

The results presented in this chapter have provided backgrounds for a computational strategy to systematically evaluate EMSI effects on platinum clusters supported by CeO₂. The use of the Ce4*f*-core potential has allowed an exhaustive evaluation of all electronic states available, revealing energy differences up to 0.8 eV between electronic states with different numbers of Ce³⁺ cations and their positions with respect to the supported Pt cluster, establishing a stabilization of ~0.5 eV due to the transfer of up to 3 electrons towards the CeO₂(111) support.

Changes in the electronic structure of the Pt₈ cluster due to EMSI were addressed by means of pDOS and Bader charge analysis, which revealed that interface Pt atoms are the most affected by EMSI. The use of the Ce4*f*-core potential reproduces reliably the changes in the electronic structure of Pt atoms, both in terms of orbital filling and charge distribution.

Chemical properties of supported Pt clusters are also affected by EMSI, where changes in their electronic structure and charge distribution at the metal-oxide interface strengthens bonding with different adsorbates. The chemical properties at cluster sites that are not in the interface are barely changed for the different electronic states sampled. This suggests the possibility of tuning chemical properties through the electron transfer from metal particles to reducible oxide supports by changing the positively charged states of reactive metal centers.

To summarize, the Ce4*f*-core potential allows for a systematic and reliable exploration of electronic states generated due to EMSI on CeO₂ supports. The data calculated using this potential reproduces the changes in the electronic structure and chemical properties of supported metal clusters, overcoming previous convergence issues happened with the Ce4*f* electron localization when using the common Ce4*f*-valence potential.

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3.6 Publication

Systematic Characterization of Electronic Metal–Support Interactions in Ceria-Supported Pt Particles

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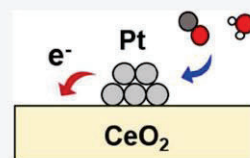
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ABSTRACT: Electronic metal–support interactions affect the chemical and catalytic properties of metal particles supported on reducible metal oxides, but their characterization is challenging due to the complexity of the electronic structure of these systems. These interactions often involve different states with varying numbers and positions of strongly correlated *d* or *f* electrons and the corresponding polarons. In this work, we present an approach to characterize electronic metal–support interactions by means of computationally efficient density functional calculations within the projector augmented wave method. We describe Ce^{3+} cations with potentials that include a $\text{Ce}4f$ electron in the frozen core, overcoming prevalent convergence and $4f$ electron localization issues. We systematically explore the stability and chemical properties of different electronic states for a $\text{Pt}_8/\text{CeO}_2(111)$ model system, revealing the predominant effect of electronic metal–support interactions on Pt atoms located directly at the metal–oxide interface. Adsorption energies and the reactivity of these interface Pt atoms vary significantly upon donation of electrons to the oxide support, pointing to a strategy to selectively activate interfacial sites of metal particles supported on reducible metal oxides.



1. INTRODUCTION

Cerium dioxide (CeO_2 , ceria) is a technologically relevant material due to its catalytic applications in fuel cells, the three-way catalysis, or the water gas shift reaction, among other reactions.^{1–6} One of the key properties of CeO_2 is its reducibility, involving the reduction of Ce^{4+} centers to Ce^{3+} upon formation of oxygen vacancies^{7–12} or electron transfer processes.^{13–16} The latter typically involve supported metal particles as electron donors, resulting in complex distortions of the electronic structure of both metal and ceria supports.^{15,17–23} The effects of these interactions on chemical properties were first identified for ceria-supported Pt particles in catalysts for the water gas shift reaction²⁴ and later coined by Campbell as electronic metal–support interactions (EMSI) in a news and views article.²⁵ EMSI are sometimes referred to as strong metal–support interactions (SMSI), which were traditionally considered as pronounced structural (instead of electronic) distortions of the metal–oxide interface detrimental to catalyst activity²⁶ but are now used more generally to describe any significant effect of the metal–support interface on reactivity.^{27,28}

EMSI are exhibited by various combinations of supports and metals,^{28–31} among which ceria-supported transition metals are frequently explored.^{32–35} Transition-metal particles often become somewhat oxidized upon contact with a reducible support such as ceria, which can affect adsorption energies and dissociation barriers of key steps within a reaction mechanism. EMSI are also markedly size-dependent, with large particles, clusters, and single atoms exhibiting different propensity for oxidation.^{19,36–38} Despite recent work elucidating some aspects of EMSI, the stability of different electronic states and the effect of the oxidation state of supported metal

particles on their chemical reactivity and catalytic properties are generally not well understood.

Theoretical calculations based on density functional theory (DFT) have led the characterization of the charge distribution and redox behavior of these systems. However, these calculations are challenging due to the strongly correlated nature of *d* and *f* electrons in some reducible oxides. A correction in the form of a Hubbard *U* or a fraction of the exact exchange is often applied to partially counteract the self-interaction error and the resulting spurious electron delocalization. These parametrized approaches are, however, not quantitatively reliable because calculated results can notably depend on the magnitude of the applied correction.³⁷ One is therefore often satisfied with describing general qualitative trends that do not disappear when varying the *U* value or the fraction of exact exchange used in the calculation.

Even when employing DFT+*U* or hybrid functionals, another important obstacle to characterizing EMSI is a challenge to carry out calculations that converge to the desired electronic state for a given system. The number and position of $4f$ electrons in Ce atoms of a ceria-based system is hard to control. In addition, many periodic codes such as VASP^{39–41} often do not converge to the most stable electronic state, and in such cases, sampling of various states is required. To

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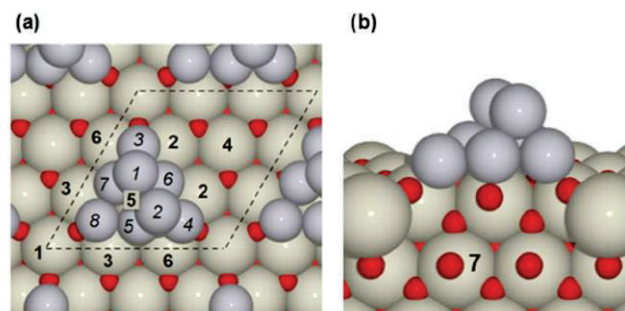


Figure 1. Structural model of the Pt_8 cluster supported on the $\text{CeO}_2(111)$ surface: (a) top view and (b) side view. Dashed lines delimit the 3×3 supercell used. Pt, Ce, and O atoms are depicted in gray, beige, and red, respectively. Numbers in bold label positions of Ce atoms relative to the Pt_8 cluster. The Ce-S atom is located below the Pt_8 cluster. Ce-7 corresponds to a subsurface Ce atom. Symmetrically equivalent Ce atoms have the same label. Numbers in italics label the Pt atoms.

overcome this, some authors have developed methods within VASP^{42,43} or other codes^{44,45} to control the orbital occupancy matrix and converge to the desired state. In this work, we propose another approach to converge to the desired electronic states by considering the f electrons of ceria as fixed core electrons of the potential used within the projector augmented wave method.^{39,41,46} We demonstrate that using such pseudopotential allows characterizing the electronic structure and chemical properties of ceria-supported Pt particles without the need to consider spin polarization, which makes the systematic characterization of EMSI for these systems computationally efficient (low cost) and straightforward (easy to converge). The systematic characterization with this approach of a previously studied $\text{Pt}_8/\text{CeO}_2(111)$ model system reveals that the effects of EMSI are strongly site-dependent and that transfer of electrons from the platinum particle to the ceria support can even invert the preference for adsorption between interface and noninterface Pt sites.

2. COMPUTATIONAL METHODS AND MODELS

2.1. Computational Methods. Density functional theory calculations were performed using periodic models as implemented in the VASP software package.^{39–41} Valence states were described by plane wave basis sets with an energy cutoff of 415 eV, and the projector augmented wave (PAW) method of Blöchl⁴⁶ was used to account for the interaction between fixed core and explicitly described valence electrons. The PAW potentials used describe 2s and 2p electrons explicitly for O and 5d and 6s electrons for Pt. For Ce atoms, we used two different PAW potentials. The most used VASP potential for Ce describes 5s, 5p, 6s, 5d, and 4f electrons explicitly and is henceforth referred to as the 4f-valence potential. An alternative potential for Ce includes one 4f electron in the core to explicitly define Ce^{3+} cations in ceria. This potential is labeled as Ce_3 (11 May 2000) in the VASP pseudopotential repository and is henceforth referred to as the 4f-core potential in this article. The convergence criterion used for the electronic structure self-consistent field was 5×10^{-6} eV. The geometries were relaxed until forces acting on the atoms which were allowed to displace were smaller than 0.05 eV $\text{\AA}^{-1}$.

The PW91⁴⁷ generalized gradient approximation (GGA) exchange–correlation functional was used. To properly describe electron localization on 4f states of Ce atoms when

using the 4f-valence potential and partially correct the self-interaction error typical of semi-local exchange–correlation functionals, we employed the GGA+U approach.⁴⁸ This introduces an energy penalty on states with partial occupation of Ce4f orbitals. For consistency with previous studies dealing with ceria-supported clusters and formation of Ce^{3+} cations,^{36,49–51} we used a U value of 4 eV.

As stated in the Introduction section, converging calculations with the desired number and position of Ce^{3+} cations is challenging even when using the GGA+U scheme. To overcome this, previous studies have carried out structural relaxations using the 4f-core potentials to precondition the structure such that a posterior (and presumably more accurate) calculation with 4f-valence potentials converges to the desired electronic state more easily. Often, but not always,⁵² energies resulting from this preconditioning procedure have been discarded in favor of those obtained in posterior calculations without constraining a selected number of 4f electrons to the corresponding Ce cores. However, the adequacy of the 4f-core potentials for describing the relative energies, electronic structure, and chemical properties of ceria-based systems has not been addressed. Therefore, in this work, we evaluate properties of ceria-supported Pt particles in various electronic states differing in the number and position of the Ce^{3+} cations obtained both with and without 4f-core potentials and propose a general approach to evaluate EMSI directly via calculations using 4f-core potentials.

We calculated the relative energies of different electronic states, the corresponding atomic charges (based on a Bader analysis⁵³) on the metal atoms of the supported Pt particle, and the reactivity of these atoms toward adsorption of catalytically relevant species. Using the 4f-core potentials straightforwardly allows us to obtain any electronic state and circumvent challenging convergence issues regarding the localization of Ce4f electrons. These convergence problems are particularly prevalent for metastable minima, for which Ce4f orbitals often change their occupation during structural relaxation.

Another advantage of using Ce4f-core potentials is that spin-polarized calculations are not required to describe the localized 4f electron fixed in the core. We can therefore characterize the desired electronic states in a computationally efficient way. Spin-restricted calculations, however, disregard such aspects as the magnetization often exhibited by supported metal particles

or the magnetic coupling between Ce4f electrons. We therefore validated selected results also with spin-polarized calculations.

2.2. Structural Models. To represent ceria-supported Pt particles, we used a periodic slab model with a Pt₈ cluster supported on the CeO₂(111) surface as shown in Figure 1. The CeO₂(111) slab is formed by 3 O–Ce–O trilayers, atomic positions in the lower of which were kept fixed during structural relaxations. This slab thickness has been shown to be sufficient in previous studies of oxygen vacancy formation on the CeO₂(111) surface.^{10,12} The experimental lattice parameter of ceria, 5.41 Å,^{54,55} was used to construct the slab. This is 0.08 Å smaller than the equilibrium lattice parameter predicted with the PW91+*U* (*U* = 4 eV) level of theory employed in the present study.

The chosen 3 × 3 supercell size offers a good compromise between the computational cost and the particle density, with distances larger than 5.9 Å between Pt₈ particles in neighboring cells. This supercell also provides a manageable number of possible configurations with different numbers and positions of Ce4f electrons (Ce³⁺), which facilitates their systematic and exhaustive characterization. Namely, for states resulting from one electron transferred to ceria (i.e., with one Ce³⁺ cation formed), there are 6 different electronic states possible corresponding to 6 inequivalent surface Ce³⁺ positions; for two transferred electrons, there are 18 different states; and for three transferred electrons, there are 35 different states. We also carried out benchmark calculations with a larger (and more computationally costly) 4 × 4 supercell (see Figure S1) to evaluate how the results change upon reducing the Pt particle coverage and increasing the distance between the particles in neighboring cells (from ~6 to ~10 Å). However, all results presented henceforth correspond to the 3 × 3 slab model of ceria unless explicitly stated otherwise.

3. RESULTS AND DISCUSSION

3.1. Relative Energies of the Electronic States of Pt₈/CeO₂(111). We begin by evaluating the effect of combining Ce4f-core and Ce4f-valence potentials (the scheme is hereafter called 4f-core) instead of using only 4f-valence potentials (4f-valence scheme) on the calculated relative energies of different electronic states of CeO₂(111)-supported Pt₈.

First, the total energy $E_{\text{tot}}^{\text{4f-core}}$ of all possible electronic states with a different number (from 0 to 3) and position of the Ce4f electrons is calculated using the 4f-core potential for the atoms selected to be Ce³⁺ cations. This provides relative energies for states with the same number of Ce³⁺ cations but does not allow comparing states with different number of atoms described with the 4f-core potential. Since previous modeling studies addressing reduced ceria surfaces and nanoparticles^{56–58} have shown that the reduction of surface Ce⁴⁺ cations is preferred to those in more bulk-like positions, we have sampled electronic states with Ce³⁺ cations in the outermost Ce layer only. However, to validate this approach, we also evaluated the stability of an electronic state with a single Ce³⁺ cation in a subsurface position.

To establish the relative energy of states with different number of transferred electrons and to assess the relative energies calculated with the 4f-core potential, we calculated the total energy $E_{\text{tot}}^{\text{4f-valence}}$ of several electronic states using the 4f-valence potentials only. All calculated relative energies ΔE are presented in Figure 2, where black and red lines indicate values calculated with ($\Delta E^{\text{4f-core}}$) and without ($\Delta E^{\text{4f-valence}}$) the Ce4f-

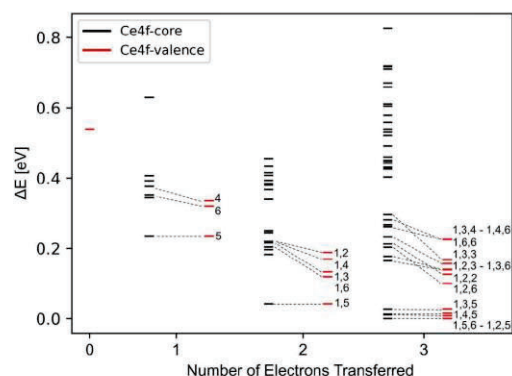


Figure 2. Relative energies $\Delta E^{\text{4f-valence}}$ and $\Delta E^{\text{4f-core}}$ of all possible electronic states calculated for the Pt₈/CeO₂ system with 0 to 3 electrons transferred from Pt₈ to the CeO₂ support. Black bars correspond to $\Delta E^{\text{4f-core}}$ values obtained using the Ce4f-core potential (with Ce4f electrons in the fixed core of selected Ce atoms) and spin-restricted calculations. Red bars correspond to $\Delta E^{\text{4f-valence}}$ values obtained using the Ce4f-valence potential only (without core Ce4f electrons) and spin-unrestricted calculations. Numbers next to red bars specify positions of the Ce³⁺ cations as labeled in Figure 1. Dashed lines connect values for states with Ce³⁺ cations in the same positions calculated using 4f-core and 4f-valence schemes. All calculated relative energy values are provided in Table S1.

core potential, respectively. $\Delta E^{\text{4f-valence}}$ values are calculated with respect to the $E_{\text{min}}^{\text{4f-valence}}$ of the most stable state found ($E_{\text{min}}^{\text{4f-valence}}$), i.e., the global minimum according to the 4f-valence scheme. $\Delta E_{i,n}^{\text{4f-core}}$ of a state *i* with *n* transferred electrons is calculated as

$$\Delta E_{i,n}^{\text{4f-core}} = E_i^{\text{4f-core}} - \Delta E_{\text{min},n}^{\text{4f-core}} + E_{\text{min},n}^{\text{4f-valence}} - \Delta E_{\text{min}}^{\text{4f-valence}}$$

where $\Delta E_{\text{min},n}^{\text{4f-core}}$ is the lowest $E^{\text{4f-core}}$ among states with the same number *n* of Ce4f electrons and $E_{\text{min},n}^{\text{4f-valence}}$ is the $\Delta E^{\text{4f-valence}}$ of that same state. We recall that it is not always possible to converge to the desired electronic state without using 4f-core potentials, particularly for unstable states. For such cases, calculations often instead converge to other states with a more favorable number or position of the Ce4f electrons.

The data in Figure 2 and Table S1 reveal that the energy differences between electronic states strongly depend on both the number and position of the Ce4f electrons. $\Delta E^{\text{4f-core}}$ for the same number of Ce³⁺ can be as high as 0.82 eV (for 3 transferred electrons), and the highest and the lowest energies calculated among all possible Ce4f electron distributions correspond to states with three transferred electrons. The most stable state is that with 3 transferred electrons from the Pt₈ particle to the ceria surface. The most stable states with two, one, and zero transferred electrons have $\Delta E^{\text{4f-valence}}$ of 0.03, 0.22, and 0.54 eV, respectively. The presence of several quasi-degenerate states within ~0.2–0.3 eV and differing in the number and position of Ce³⁺ cations suggest a facile mobility of electrons between different Ce ions and the supported Pt₈ particle. EMSI for this system are thus expected to involve a significant dynamic behavior, similarly to ceria-

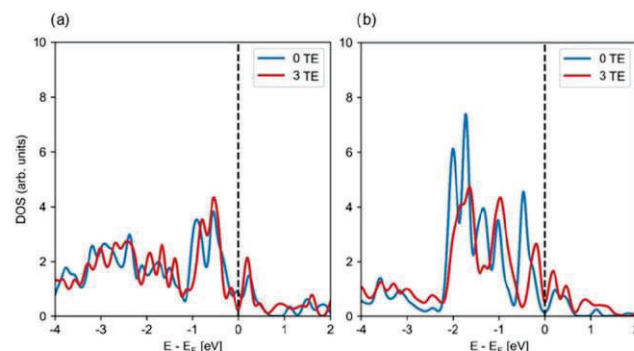


Figure 3. Density of states (DOS) projected on (a) Pt-1 second-layer and (b) Pt-8 interface atoms (as labeled in Figure 1) of the Pt_8 cluster supported on the $\text{CeO}_2(111)$ surface for the most stable electronic state (3 electrons transferred) and the state without electrons transferred from the metal to the oxide. The data are calculated spin-unrestricted using the 4f-valence potential only. Energies are shifted with respect to the Fermi level, which is indicated by a vertical dashed line.

supported Pt atoms³⁷ or Au particles.⁵⁹ We note that the $E_{\text{4f-core}}^{\text{Ce}^{3+}}$ of the electronic state with a single Ce^{3+} cation in a subsurface position is 0.39 eV larger than the $E_{\text{4f-core}}^{\text{Ce}^{3+}}$ of the most stable state found with one transferred electron. This implies that the sampling of electronic states with Ce^{3+} cations in subsurface positions is not necessary.

The relative energies $\Delta E_{\text{4f-valence}}^{\text{Ce}^{3+}}$ calculated with unrestricted spin and Ce4f-valence potentials (red bars in Figure 2) are smaller than the corresponding energies $\Delta E_{\text{4f-core}}^{\text{Ce}^{3+}}$ calculated with restricted spin using Ce4f-core potentials (black bars in Figure 2). The larger energy differences obtained with the Ce4f-core potentials may be attributed to disregarding the magnetic coupling between the Ce4f electrons or to the slightly stronger ionic character of Ce^{3+} cations when described with a fixed 4f electron. Apparently, the fixed electron cannot participate in the polar covalent Ce–O bonding, leading to a slightly higher atomic charge (by ~ 0.01 – 0.03 |e|) and stronger electrostatic interaction. However, the 4f-core and 4f-valence approaches agree in the most stable electronic states, with changes (or crossings) in the stability order found for states mostly with large $\Delta E_{\text{4f-core}}^{\text{Ce}^{3+}}$ and $\Delta E_{\text{4f-valence}}^{\text{Ce}^{3+}}$ values (Figures 2 and S2). We also note that considering spin polarization has little effect on calculated $\Delta E_{\text{4f-core}}^{\text{Ce}^{3+}}$ values, with differences ≤ 0.02 eV per transferred electron (see Table S1). The $\Delta E_{\text{4f-valence}}^{\text{Ce}^{3+}}$ values calculated with the 4×4 supercell are in good agreement with those obtained with the 3×3 supercell (Figure S3, Table S2). Using the 4×4 supercell, energy differences between the most stable electronic states with two transferred electrons and the states with one and zero transferred electrons are 0.23 and 0.54 eV, respectively. These energy differences are 0.22 and 0.55 eV, when using the 3×3 supercell.

From the calculated relative energies, some trends can be identified regarding the formation of Ce^{3+} cations in $\text{Pt}_8/\text{CeO}_2(111)$. Electron transfer from the supported Pt_8 cluster is favored to Ce^{4+} cations in closer contact to the cluster (see labels in Figures 1 and 2). We attribute this to the additional space created around Ce atoms upon the formation of Pt–O bonds. The latter weaken and elongate the corresponding Ce–O bonds, thus facilitating the presence of Ce^{3+} cations, which have characteristically larger ionic radii than Ce^{4+} (see Table S3). For the most favorable position for forming Ce^{3+} (position 5, Figure 2), the 3 Ce–O bonds at the surface

extend to 2.45 Å vs 2.35 Å of Ce–O in the bare surface. Ce-1 is another very favorable position for hosting a 4f electron because of its proximity to three neighboring Pt_8 clusters resulting in extended Ce–O bonds. The most stable Ce^{3+} distributions for states with more than one transferred electron also involve this position. We also note that the Ce^{3+} –O distances predicted with the 4f-core or 4f-valence approaches are in very good agreement (see Table S3). This is unsurprising given that the 4f-core potential of Ce has been traditionally used not to directly model desired polaronic states in reduced ceria but rather to precondition the structures in a prerelaxation calculation. This facilitates the convergence to the desired electronic state in a posterior relaxation with the 4f-valence approach.

Ce^{3+} cations also avoid being immediate neighbors, in agreement with previous work^{10,12} dealing with the characterization of oxygen vacancies in reduced ceria. For example, once a Ce^{3+} is formed in position Ce-5 (below the cluster), reducing one of the neighboring Ce^{4+} cations (Ce-2 or Ce-3) is less favorable than reducing Ce^{4+} cations in other sites.

The calculated relative energies indicate that Ce4f-core potentials can be used to quite reliably identify stable electronic states in systems involving reduced ceria. Considering the more facile convergence to the desired electronic state and the possibility to use spin-restricted calculations, this approach enables the systematic and computationally efficient characterization of EMSI.

3.2. Effect of EMSI on the Electronic Structure of Pt_8 Supported on $\text{CeO}_2(111)$. To evaluate the EMSI effect on the electronic structure of the $\text{CeO}_2(111)$ -supported Pt_8 cluster, we compare the projected density of states (pDOS) and atomic Bader charges for several electronic states described in the previous section differing in the number and position of Ce^{3+} centers (i.e., in the number of electrons transferred from the Pt_8 cluster and the position of the Ce^{4+} cations that the transferred electrons reduce). We also evaluate the differences between results obtained using the 4f-core potential (to describe Ce^{3+} centers) and spin-restricted calculations to those calculated with spin polarization with the 4f-valence potential. However, we note that the spin-restricted and spin-unrestricted calculations using the 4f-core

potential yield practically identical pDOS for the supported Pt₈ clusters (see Figure S4).

The added pDOS of all atoms of the Pt₈ cluster for the states with 0, 1, 2, and 3 transferred electrons is shown in Figure S5, although a straightforward analysis of the differences is challenging. We therefore focus instead on the changes in pDOS projected on individual Pt atoms upon the transfer of electrons from Pt₈ to CeO₂(111), namely, an interface Pt atom and a second-layer Pt atom (Pt-8 and Pt-1 in Figure 1, respectively). Results of spin-polarized calculations with Ce4f-valence potentials in Figure 3 allow us to compare the state with no transferred electrons to the most stable state obtained featuring three transferred electrons and reduced Ce-1, Ce-5, and Ce-6 centers.

The pDOS of the interface atom and the second-layer atom are different regardless of the electronic state, which reflects an inhomogeneous charge distribution within the supported Pt₈ cluster similarly to ceria-supported Au particles.⁵⁹ Interestingly, there are only little differences in the pDOS of the second-layer Pt (Pt-1, Figure 3a) between the two electronic states, whereas the intensities and positions of the pDOS peaks differ notably for the interface Pt atom (Pt-8, Figure 3b). Therefore, the charge redistribution upon electron transfer is also inhomogeneous and has a stronger effect on interface atoms. As we show below, this is also reflected in the atomic charges and the chemical properties of these Pt atoms.

We have also calculated the pDOS for systems with the same number but different positions of Ce³⁺ cations, revealing that the exact location of the Ce4f electrons has a small effect on the electronic structure of the supported particles (see Figure S6). Thus, despite the effect of such positions on the stability of the Pt₈/CeO₂(111) models, the electronic structure of supported Pt particles is noticeably affected only by the number of transferred electrons.

Integration of the DOS projected on different orbitals of the atoms in the Pt₈ particle reveals a lower number of occupied *d* states but a higher number of occupied *sp* states (see Table S3) upon electron transfer to the oxide surface. This indicates that electrons are transferred from Pt *d* orbitals to ceria, with a concomitant back-donation of electrons to the Pt *sp* states. The values for the integrated pDOS of all states of Pt evolve erratically with the number of Ce³⁺ centers, with an abnormally large value for the state with two transferred electrons. Despite this, atomic charges on the Pt₈ cluster evolve as expected and become progressively larger upon the transfer of every additional electron (*vide infra*).

The inhomogeneous charge distribution and nonuniform effect of electron transfer on interface and second-layer atoms of the Pt cluster is also reflected on the corresponding atomic Bader charges (see Figure 4 and Table S4). For all states, interface Pt atoms are more oxidized (i.e., carry larger positive Bader charges) than second-layer Pt atoms. Comparison of Bader charges of atoms with different coordination should, however, be carried out with care. The larger Bader volume assigned to less coordinated atoms can lead to more negative Bader charges on them, even for systems where a polarization is not expected. It is more reliable to analyze variations of the Bader charges upon a given process. For example (Table S4), the total charge of the Pt₈ cluster is, as expected, larger for more oxidized states. The electronic states with zero, one, two, and three transferred electrons exhibit total Pt₈ cluster charges of 0.25, 0.49, 0.70, and 1.03 lel, respectively. The majority of this 0.78 lel variation involves interface Pt atoms, whose charge

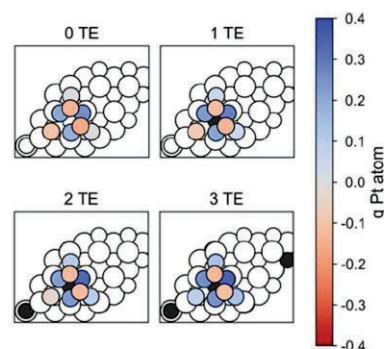


Figure 4. Bader charges (*q*) of atoms in the Pt₈ cluster supported on CeO₂(111) for most stable electronic states with 0–3 transferred electrons (TE) from the Pt cluster to the oxide. Pt atoms are colored according to their Bader charges, as indicated in the colorbar: red—negative charge and blue—positive charge. Black circles depict Ce³⁺ cations. The corresponding values are also given in Table S4.

increases by 0.06 to 0.21 lel. In contrast, the charges of the second-layer atoms Pt-1 and Pt-2 remain nearly constant. Thus, EMSI and related electron transfer in CeO₂-supported Pt particles are expected to affect the chemical properties mainly of the interface metal atoms. Similar to what was observed for the pDOS, the Bader charge of the Pt atoms is also hardly sensitive to the position of the Ce³⁺ centers and mainly depends on the number of transferred electrons (Table S5). The electronic structure of the supported Pt particle is also insensitive to the particle coverage decrease, with almost identical pDOS (see Figure S7) and Bader charges (see Table S6). Thus, the shorter distances between Pt particles have a negligible effect on the relative stability of different electronic states, the atomic charges of the Pt atoms, and the orbital energies of the Pt particle.

The effect of electron transfer is also reflected in structural changes of the Pt₈/CeO₂(111) model. More positive charges of the Pt atoms at the interface lead to a shortening of the corresponding Pt–O bonds (Table 1). This is attributed to

Table 1. Pt–n–O Bond Lengths between the Pt–*n* Atom and the Nearest O Atoms of the CeO₂(111) Surface Calculated for Electronic States with 0 to 3 Transferred Electrons (TE) from Pt₈ to CeO₂^a

Pt– <i>n</i> –O [Å]	0 TE	1 TE	2 TE	3 TE
Pt-3	2.07	2.06	2.02	2.00
Pt-4	2.07	2.06	2.02	2.00
Pt-5	2.02	2.02	2.02	2.00
Pt-6	2.01	2.00	1.99	1.98
Pt-7	2.02	2.02	2.02	2.00
Pt-8	2.09	2.08	2.04	2.02

^aNumbers *n* are the labels of Pt atoms in Figure 1.

strengthening of such bonds induced by the decrease in occupation of antibonding Pt5*d* states upon partial oxidation. As we show below, these electronic effects also lead to stronger bonding with different adsorbates.

The strengthening of the Pt–O bonds upon increasing cationic character of Pt atoms is consistent with the relative energies reported in Figure 2, where the states with more

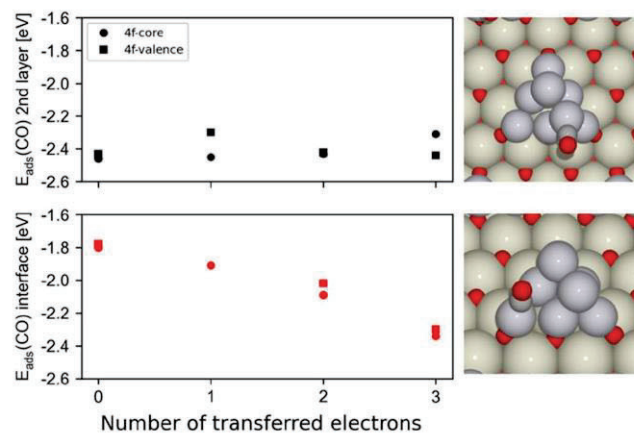


Figure 5. CO adsorption energies on the interface (Pt-8) and second-layer (Pt-1) atoms of the Pt_8 cluster supported on $\text{CeO}_2(111)$ for the electronic states with 0–3 electrons transferred from Pt_8 to CeO_2 . Data calculated using the 4f-core, spin-restricted approach are shown by circles, and those calculated using the 4f-valence, spin-unrestricted method are shown by squares. The two evaluated CO adsorption sites (on-top interface and on-top second layer) are illustrated in the right-hand panels, which show the relaxed structures for the electronic state without any transferred electrons.

oxidized Pt (less occupied antibonding $\text{Pt}5d$ orbitals) are more stable than the states with more metallic Pt.

Finally, using the $\text{Ce}4f$ -core potential to describe Ce^{3+} cations and spin-restricted calculations has a negligible effect also on the Bader charges of the Pt_8 cluster. This, together with the above results on pDOS of Pt atoms, justifies that the more computationally efficient 4f-core approach can reliably describe the electronic structure of different states of ceria-supported Pt particles.

3.3. Chemical Properties of the Pt_8 Cluster in Different Electronic States. We have characterized the effects of EMSI on the reactivity of different sites of the ceria-supported Pt_8 particle. In particular, we considered the adsorption of common adsorbates CO, H_2O , OH, and H calculated at two DFT levels, i.e., with and without describing Ce^{3+} cations with the 4f-core potential. The adsorption energies E_{ads} are defined as

$$E_{\text{ads}} = E(\text{adsorbate}/\text{Pt}_8/\text{CeO}_2) - E(\text{Pt}_8/\text{CeO}_2) - E(\text{adsorbate})$$

where $E(\text{adsorbate}/\text{Pt}_8/\text{CeO}_2)$ and $E(\text{Pt}_8/\text{CeO}_2)$ are the total energies of the models with and without the adsorbate, respectively. $E(\text{adsorbate})$ is the energy of the gas-phase adsorbate species, i.e., $E(\text{CO})$, $E(\text{H}_2\text{O})$, $E(\text{OH})$, or $1/2E(\text{H}_2)$. E_{ads} values are calculated for adsorbate/ Pt_8/CeO_2 and Pt_8/CeO_2 states with the same number and positions of Ce^{3+} cations, i.e., assuming that the oxidation state of the Pt_8 particle and underlying oxide is preserved upon adsorption. This allows examining the chemical properties for every individual electronic state under scrutiny. We considered the adsorption on the Pt-8 interface and Pt-1 second-layer atoms, for the electronic states with zero to three transferred electrons probing on-top adsorption geometries. For CO, OH, H_2O , and H, the on-top site of a second-layer atom is the most favorable adsorption site for the electronic state without any transferred electrons, with bridge or hollow sites being less stable. For interface Pt atoms, the on-top site is the most favorable

adsorption site for CO, OH, and H_2O , whereas for H, the bridge site between an interface and a second-layer atom is more favorable. Nevertheless, we only consider on-top sites in our comparison to suppress effects emerging from differences in site symmetry. Note that we locally reoptimize (relax) the structure for every combination of electronic state, site, and adsorbate.

The adsorption energies of a single CO molecule on-top of the two selected Pt-8 and Pt-1 sites are shown in Figure 5 and Table S7, revealing clear differences for different sites, as well as a markedly different evolution with the number of transferred electrons. For the electronic state without any transferred electrons, CO adsorption is 0.65 eV stronger on the second-layer site, whereas the adsorption energies are almost identical for the electronic state with three transferred electrons. In agreement with the more pronounced changes in the electronic structure of the interface Pt atoms due to Pt_8 – CeO_2 charge transfer, the reactivity of the interface sites is also more strongly modified upon oxidation of the particle and concomitant reduction of the ceria surface. Thus, not unexpectedly, EMSI mainly affect the chemical properties of the interface metal atoms, which could be tuned by controlling the number of transferred electrons.

CO adsorption energies obtained using the 4f-core, spin-restricted approach agree well with the energies using the 4f-valence and spin-unrestricted level of theory. E_{ads} trends are well reproduced, and the E_{ads} differences between these two approaches range only from 0.02 to 0.10 eV. These E_{ads} differences are mainly due to treating the $\text{Ce}4f$ electron as a part of the core, whereas the energy differences between the spin-restricted and spin-unrestricted calculations are minor (see Table S7). Some states, such as that for one transferred electron and CO adsorbed on the interface site, can only be obtained using the 4f-core potential, with calculations converging to other electronic states when using the 4f-valence potential only. In turn, states without any transferred electrons can obviously only be obtained without the 4f-core potential, and we therefore just use spin-restricted calculations with the

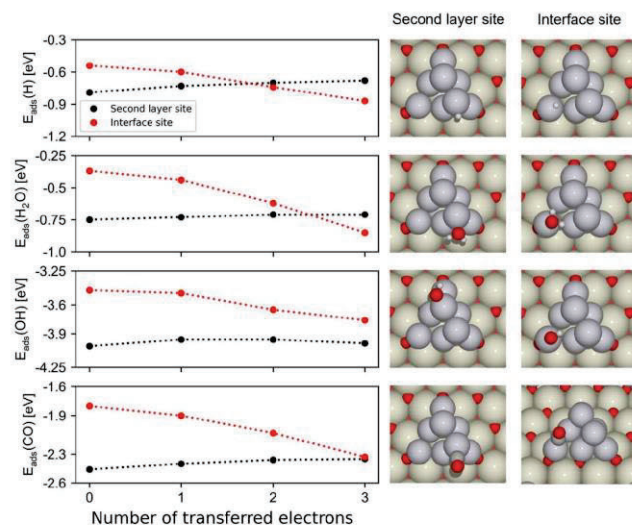


Figure 6. Adsorption energies of H, H₂O, OH, and CO adsorbates on Pt₈/CeO₂(111) for the most stable electronic states with different number of electrons transferred from the metal cluster to the oxide support. The black and red markers correspond to adsorption energies of adsorbates in on-top positions at the second-layer and interface sites of Pt₈, respectively. The two evaluated sites for every adsorbate (on-top interface and on-top second layer) are illustrated in the right-hand panels, which show the relaxed structures for the electronic state without any transferred electrons. The corresponding energy values are also reported in Table S9.

4f-valence potentials to complete the 4f-core series. Finally, the just discussed $E_{\text{ads}}(\text{CO})$ values calculated with the ceria supercell 3×3 change only moderately, by up to 0.1 eV, when using a larger supercell 4×4 (see Table S8).

The good established performance and accuracy of the spin-restricted calculations using the 4f-core potential for describing Ce³⁺ cations open a way to reliably and systematically evaluate E_{ads} trends across different adsorbates (H, OH, H₂O), sites (interface and second layer), and electronic states (from zero to three transferred electrons); see Figure 6 and the data in Table S9.

In the absence of transferred electrons, adsorption on the interface site is weaker than on the second-layer site for all adsorbates considered in the present work. As was the case for the adsorbed CO, adsorption of H, H₂O, and OH on the interface site becomes stronger upon electron transfer from the metal particle to the ceria surface, whereas adsorption energies on the second-layer site remain almost unchanged. The different evolution of the adsorption strength on the interface and second-layer sites with electron transfer even leads to an inversion in preferred adsorption site for H₂O and H. Thus, EMSI significantly affect adsorption properties of interface sites for various adsorbates. More specifically, the variation from zero to three transferred electrons strengthens the adsorption of H, H₂O, OH, and CO by 0.3, 0.5, 0.3, and 0.5 eV, respectively. This stronger adsorption can also be considered as a pronounced stabilization upon exposure to reactants of electronic states with oxidized Pt vs less oxidized states of Pt. Ceria-supported Pt particles are therefore expected to donate more electrons to the oxide support when adsorbates interact with interface atoms of the Pt particles. Surprisingly, the bond distances between the adsorbate and Pt and between atoms of the adsorbate (e.g., the C–O bond) are not affected by the number of transferred electrons. This suggests that the effect of

electron transfer on the adsorption energies is to a significant extent due to a peculiar stabilization of some electron configurations in the presence of an adsorbate. As discussed below, we hypothesize that electrostatic interactions between Ce³⁺ centers and the interface Pt atom play an important role.

The demonstrated dependence of the adsorption properties of Pt atoms at the Pt/CeO₂ interface on the number of transferred electrons indicates that the affinity of these sites toward reactants and intermediates can be tuned by controlling the reducibility of the ceria support. More reducible ceria-based supports such as ceria nanoparticles^{9,11} or some doped ceria materials^{60–62} will lead to more oxidized Pt particles and, therefore, to stronger interaction with the interface Pt atoms. In turn, ceria supports with a high concentration of oxygen vacancies (i.e., very reduced) and saturated with Ce4f electrons would less favorably accept electrons from Pt, stabilizing more reduced Pt states and leading to weaker interactions between adsorbates and interface Pt atoms. A similar picture was reported for ceria-supported Au particles, where reduction of ceria led to charge redistribution and the transfer of electrons back to the supported Au particles.⁵⁹

We have shown above that the electronic structure (pDOS and Bader charges) of both the interface and second-layer Pt sites essentially does not depend on the position of Ce³⁺ centers (only on the concentration of the latter). Interestingly, CO adsorption energies at the interface Pt site noticeably depend on the individual Ce³⁺ positions (see Figure S8a and b). We attribute this to the fact that Pt atoms donate a significant amount of charge to form Pt–CO bonds, leading to more positively charged Pt atoms. Since the electrostatic repulsion of such Pt^{δ+} atoms is weaker from Ce³⁺ than from Ce⁴⁺ cations, it stabilizes the CO–Pt^{δ+}–Ce³⁺ motif vs the CO–Pt^{δ+}–Ce⁴⁺ one. This effect is stronger for the 4×4 supercell, where adsorption energy differences for states with

different Ce^{3+} positions can be as high as 0.34 eV (Figure S8c and d).

Inhomogeneous charge distributions have been reported for other transition-metal particles (Ni, Cu, Au) supported on reducible oxides such as CeO_2 and TiO_2 ,^{29,30,63,64} where interface atoms experience more pronounced charge depletion than those farther away from the support. CO adsorption on ceria-supported Cu particles was also calculated to be site-sensitive, with an adsorption energy of 0.72 eV for Cu^0 and 0.79 eV for Cu^+ sites.⁶³ A similar trend favoring adsorption on cationic metals was found for Au atoms on CeO_2 , where the adsorption energy of CO is 2.48 eV on Au^+ sites and 3.24 eV on Au^{3+} sites.³⁴ For Pt_8 particles supported on CeO_2 nanoparticles, CO adsorption was reported to be weaker on interface sites in contact with ceria,⁶⁵ in line with the present work. This supports previous observations that vibrational frequencies of CO on small Pt clusters supported on nonreducible oxides are dependent on the oxidation state of the adsorption site.⁶⁶ The strengthening of CO–Pt interactions on the interface site of the ceria-supported Pt_8 cluster with increased electron transfer to ceria calculated using the 4f-valence approach¹⁵ is in quantitative agreement with the 4f-core data in Table S9. Thus, the explanation therein of the quite unexpected trend is also partially applicable to the present work. In particular, they report that the main contribution to the stronger CO adsorption comes from the increased σ -donation to Pt with an unchanged 2π back-donation.¹⁵ We note in passing that the employed 4f-valence approach hindered convergence for H_2O adsorption on the interface site of ceria-supported Pt_8 at 2 TE,¹⁵ which did not present a problem within the present 4f-core approach. An opposite dependence of the CO adsorption energy on the charge was calculated for ceria-supported Ni, 1.90 eV on metallic and cluster Ni^0 and 1.39 eV on single-atom Ni^{2+} sites.⁶⁷

The interplay between adsorption energy and charge distribution in the supported catalyst points to the possibility of tuning the chemical reactivity of oxide-supported metal clusters by controlling the oxidation state of reducible oxide supports. Reducing or oxidizing oxide supports would modify their propensity to accept or donate electrons, thus favoring different adsorption sites in supported clusters. Still, it is not clear yet to what extent this electron transfer process depends on the morphology of the metallic nanostructure (single atoms, clusters, nanoparticles, or monolayers) and the reductive capacity of different facets of reducible supports.⁶⁸

4. CONCLUSIONS

In this work, we have systematically evaluated the effects of EMSI on the properties of ceria-supported Pt particles. We have identified a plethora of electronic states close in energy but differing in the number of transferred electrons from the Pt particle to the underlying oxide surface and in the position of the reduced Ce^{3+} cations. The most stable electronic state found exhibits three transferred electrons, which is over 0.5 eV more stable than the state without transferred electrons. The stability of 4f electrons on different Ce positions is mainly related to the available space around each Ce atom, which is in general increased by the formation of Pt–O bonds.

Despite the effect of the position of the Ce4f electrons on the stability of the system, the electronic structure of the Pt atoms of the particle is only noticeably affected by the number of transferred electrons, leading to less filled d states and more

positive Bader charges. Interaction with the ceria support oxidizes interface atoms more significantly, and the charge redistribution upon transfer of electrons affects mainly these Pt atoms located directly at the metal–oxide interface.

The electronic structure changes of the interface Pt atoms significantly affect their chemical properties, strengthening bonds with all evaluated adsorbates (CO , H_2O , H , and OH) upon transfer of electrons from Pt to ceria. This strengthening is attributed to less occupied antibonding Pt5d orbitals on these sites and partially also to weaker electrostatic interactions between positively charged Pt and nearby Ce^{3+} centers. The different reactivity evolution of the interface and the second-layer sites upon transfer of electrons to the support suggests that different sites can be selectively activated by controlling the state of the ceria support, which would accept fewer electrons from Pt particles when already saturated with Ce4f electrons.

Finally, we have demonstrated that the approach used in this work relying on the Ce PAW potential with a fixed core 4f electron (i.e., the 4f-core potential) to describe selected Ce atoms as Ce^{3+} cations allows one to systematically and reliably probe the electronic structure and reactivity of multiple electronic states emerging from the EMSI in ceria-supported Pt particles. Overcoming the known convergence issues and localization challenges of the Ce4f electron with this 4f-core approach therefore makes the characterization of such complex interactions in ceria-supported metal species straightforward and computationally efficient.

■ ASSOCIATED CONTENT

Data Availability Statement

The outputs from the calculations underlying this study are openly available in ioChem-BD repository at <http://dx.doi.org/10.19061/iochem-bd-6-271>.⁶⁹

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c03383>.

Structural model of the $\text{Pt}_8/\text{CeO}_2(111)$ model using a $4 \times 4 \times 4$ $\text{CeO}_2(111)$ supercell; tabulated and plotted relative energies of electronic states with different numbers and positions of transferred electrons from Pt_8 to $\text{CeO}_2(111)$; tabulated Ce–O bond distances of relevant structures; DOS plots for different electronic states of the $\text{CeO}_2(111)$ -supported Pt_8 cluster; Bader charges and integrated pDOS of the Pt_8 cluster; tabulated adsorption energy values for CO, H_2O , H , and OH on Pt_8/CeO_2 ; and illustration of the effect of the positions of reduced Ce^{3+} centers on the stability of adsorbed CO (PDF)

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Notes

The authors declare no competing financial interest.

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Supplementary information for:

**Systematic Characterization of Electronic Metal Support
Interactions in Ceria-supported Pt Particles**

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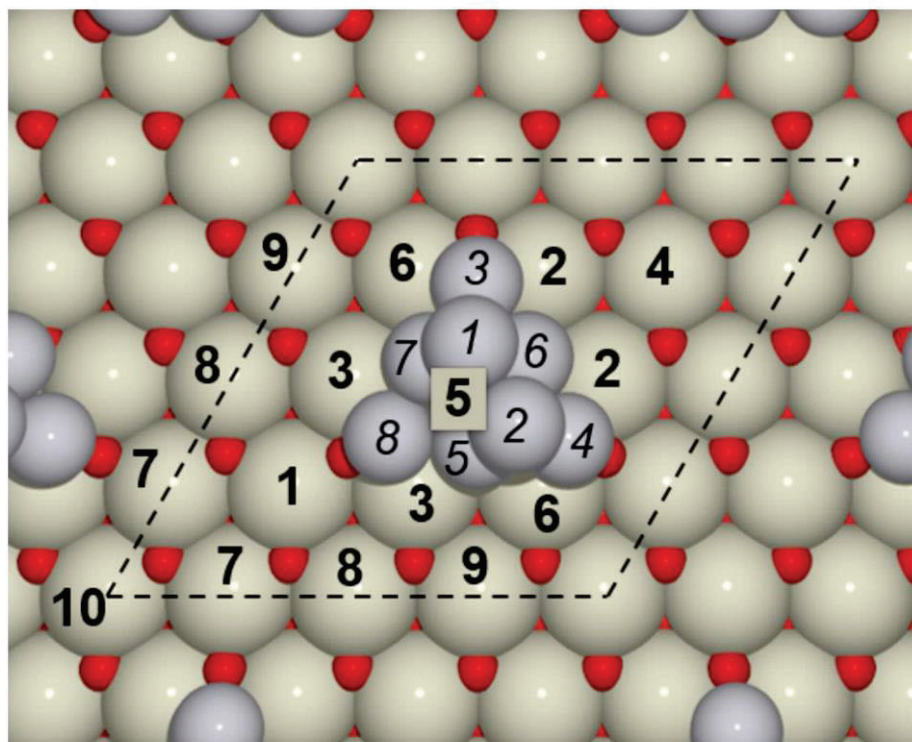


Figure S1: Structural model of a Pt_8 cluster supported on the $\text{CeO}_2(111)$ surface. Dashed lines delimit the 4×4 supercell used. Pt, Ce and O atoms are depicted in grey, beige, and red, respectively. Numbers in bold are labels of Ce atoms according to their position relative to the Pt_8 cluster. Ce-5 atom is located below the Pt_8 cluster. Symmetrically equivalent Ce atoms have the same label. Numbers in italics are labels of the Pt atoms.

System	$\Delta E_{rel}^{4f-core}$	$\Delta E_{rel}^{4f-valence}$	System	$\Delta E_{rel}^{4f-core}$	$\Delta E_{rel}^{4f-valence}$
0 TE	-	0.54	3 TE - 1,3,3 ($\uparrow\uparrow\uparrow$)	0.19	0.15
1 TE - 1	0.32	-	3 TE - 1,3,4 ($\downarrow\uparrow\uparrow$)	0.25	0.22
1 TE - 2	0.38	-	3 TE - 1,3,5 ($\uparrow\uparrow\uparrow$)	0.03	0.02
1 TE - 3	0.39	-	3 TE - 1,3,6 ($\downarrow\downarrow\downarrow$)	0.16	0.13
1 TE - 4 ($\uparrow$)	0.36	0.32	3 TE - 1,4,5 ($\uparrow\downarrow\downarrow$)	0.01	0.01
1 TE - 5 ($\uparrow$)	0.22	0.22	3 TE - 1,4,6 ($\uparrow\uparrow\uparrow$)	0.21	0.22
1 TE - 6 ($\uparrow$)	0.34	0.3	3 TE - 1,5,6 ($\uparrow\uparrow\uparrow$)	0.00	0
1 TE - 7	0.61	-	3 TE - 1,6,6 ($\uparrow\uparrow\uparrow$)	0.26	0.16
2 TE - 1,2 ($\uparrow\uparrow$)	0.20	0.18	3 TE - 2,2,3	0.58	-
2 TE - 1,3 ($\uparrow\uparrow$)	0.23	0.12	3 TE - 2,2,4	0.68	-
2 TE - 1,4 ($\uparrow\uparrow$)	0.22	0.16	3 TE - 2,2,5	0.42	-
2 TE - 1,5 ($\uparrow\uparrow$)	0.03	0.03	3 TE - 2,2,6	0.49	-
2 TE - 1,6 ($\downarrow\downarrow$)	0.19	0.11	3 TE - 2,3,3	0.57	-
2 TE - 2,2	0.37	-	3 TE - 2,3,4	0.63	-
2 TE - 2,3	0.35	-	3 TE - 2,3,5	0.38	-
2 TE - 2,4	0.40	-	3 TE - 2,3,6	0.50	-
2 TE - 2,5	0.19	-	3 TE - 2,4,5	0.43	-
2 TE - 2,6	0.33	-	3 TE - 2,4,6	0.62	-
2 TE - 3,3	0.42	-	3 TE - 2,5,6	0.42	-
2 TE - 3,5	0.23	-	3 TE - 2,6,6	0.50	-
2 TE - 3,6	0.38	-	3 TE - 3,3,4	0.68	-
2 TE - 4,5	0.17	-	3 TE - 3,3,5	0.46	-
2 TE - 4,6	0.39	-	3 TE - 3,3,6	0.52	-
2 TE - 5,6	0.18	-	3 TE - 3,4,5	0.43	-
2 TE - 6,6	0.37	-	3 TE - 3,4,6	0.67	-
3 TE - 1,2,2 ($\uparrow\uparrow\uparrow$)	0.17	0.12	3 TE - 3,5,6	0.40	-
3 TE - 1,2,3 ($\uparrow\uparrow\uparrow$)	0.13	0.13	3 TE - 3,6,6	0.54	-
3 TE - 1,2,4	0.23	-	3 TE - 4,5,6	0.40	-
3 TE - 1,2,5 ($\uparrow\uparrow\uparrow$)	0.01	0	3 TE - 4,6,6	0.79	-
3 TE - 1,2,6 ($\uparrow\uparrow\uparrow$)	0.16	0.09	3 TE - 5,6,6	0.39	-

Table S1: Comparison of energy differences ΔE of electronic states calculated using the 4f-core scheme and the 4f-valence scheme. Energy differences are calculated separately for each number of electrons transferred. The numbers after the number of electrons transferred N TE specify the positions of N surface Ce^{3+} cations according to the labels in Fig. 1. In parenthesis are indicated the spin orientation of every Ce^{3+} cation obtained at the 4fvalence-su level, where ' $\uparrow$ ' denotes spin up and ' $\downarrow$ ' is spin down.

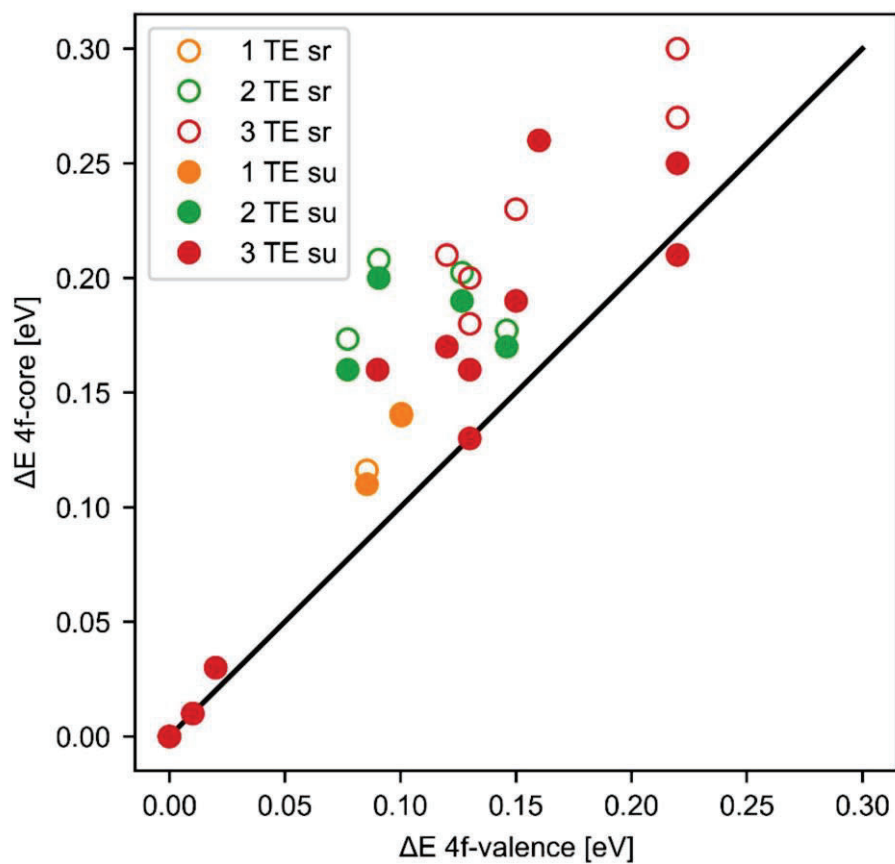


Figure S2: Dispersion of energy difference values obtained with 4f-core and 4f-valence potentials. Empty circles are energy differences obtained for spin-restricted calculations while solid circles are energy differences obtained for spin-unrestricted calculations. Energy differences are calculated separately for each number of transferred electrons TE.

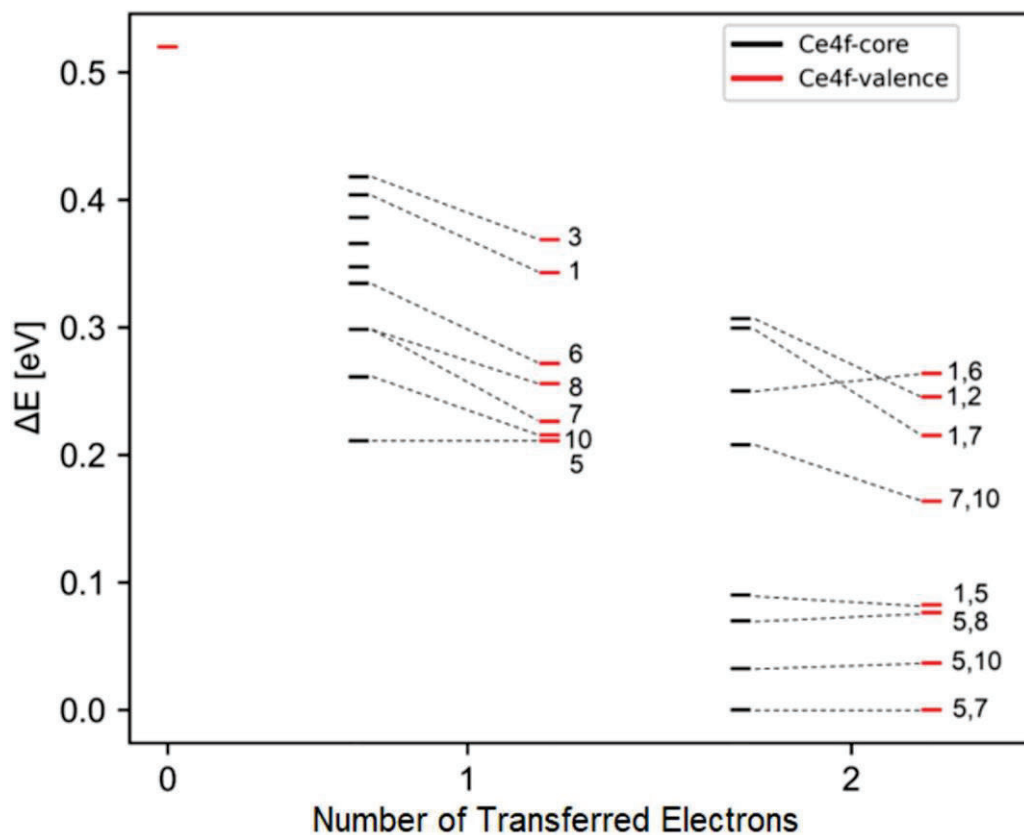


Figure S3: Relative energies $\Delta E^{4f-valence}$ and $\Delta E^{4f-core}$ of all possible electronic states calculated for the Pt_8/CeO_2 system with 0 to 2 electrons transferred from Pt_8 to the CeO_2 support with the supercell size 4×4 . Black bars correspond to $\Delta E^{4f-core}$ values obtained using the Ce4f-core potential (with Ce4f electrons in the core of selected Ce atoms) and spin-restricted calculations. Red bars correspond to $\Delta E^{4f-valence}$ values obtained using the Ce4f-valence potential only (without fixed core Ce4f electrons) and spin-unrestricted calculations. Numbers next to red bars specify positions of the Ce^{3+} cations as labeled in Figure S1. Dashed lines connect values for states with Ce^{3+} cations in the same positions calculated using the 4f-core and 4f-valence schemes. All values are also provided in Table S2.

System	$\Delta E^{4f-core}$	$\Delta E^{4f-valence}$
1 TE - 1 ($\uparrow$)	0.4	0.34
1 TE - 2	0.37	-
1 TE - 3 ($\uparrow$)	0.42	0.37
1 TE - 4	0.39	-
1 TE - 5 ($\uparrow$)	0.21	0.21
1 TE - 6 ($\uparrow$)	0.33	0.27
1 TE - 7 ($\uparrow$)	0.3	0.23
1 TE - 8 ($\downarrow$)	0.3	0.26
1 TE - 9	0.35	-
1 TE - 10 ($\uparrow$)	0.26	0.21
2 TE - 5,10 ($\uparrow\uparrow$)	0.03	0.04
2 TE - 5,7 ($\downarrow\downarrow$)	0	0
2 TE - 1,7 ($\uparrow\uparrow$)	0.3	0.22
2 TE - 5,8 ($\downarrow\uparrow$)	0.07	0.08
2 TE - 1,5 ($\uparrow\uparrow$)	0.09	0.08
2 TE - 1,2 ($\downarrow\downarrow$)	0.31	0.25
2 TE - 1,6 ($\uparrow\downarrow$)	0.25	0.26
2 TE - 7,10 ($\downarrow\uparrow$)	0.21	0.16

Table S2: Energy differences of selected electronic states of the 4×4 slab model obtained using the 4*f*-core scheme and the 4*f*-valence scheme. Energy differences are calculated separately for each number of transferred electrons. The numbers after the number of transferred electrons N TE specify the positions of N surface Ce³⁺ cations according to the labels in Fig. S1. In parenthesis are indicated the spin orientation of every Ce³⁺ cation obtained at the 4*f*-valence spin unrestricted level, where ‘ $\uparrow$ ’ denotes spin up and ‘ $\downarrow$ ’ is spin down.

Ce ³⁺ - O bond distance (surface Ce-O bonds)				Ce ³⁺ - O bond distance (sub-surface Ce-O bonds)			
		4f-core	4f-valence			4f-core	4f-valence
0 TE	Ce(5)-O1		2.457	0 TE	Ce(5)-O4		2.363
	Ce(5)-O2		2.455		Ce(5)-O5		2.353
	Ce(5)-O3		2.453		Ce(5)-O6		2.363
	Ce(1)-O1		2.368		Ce(5)-O7		2.369
	Ce(1)-O2		2.374		Ce(1)-O4		2.319
	Ce(1)-O3		2.295		Ce(1)-O5		2.322
	Ce(6)-O1		2.316		Ce(1)-O6		2.317
	Ce(6)-O2		2.299		Ce(1)-O7		2.501
	Ce(6)-O3		2.454		Ce(6)-O4		2.355
1 TE	Ce(5)-O1	2.635	2.630		Ce(6)-O5		2.344
	Ce(5)-O2	2.633	2.623		Ce(6)-O6		2.328
	Ce(5)-O3	2.603	2.592		Ce(6)-O7		2.411
2 TE	Ce(5)-O1	2.617	2.617	1 TE	Ce(5)-O4	2.445	2.419
	Ce(5)-O2	2.627	2.621		Ce(5)-O5	2.444	2.424
	Ce(5)-O3	2.621	2.607		Ce(5)-O6	2.445	2.427
	Ce(1)-O1	2.501	2.494		Ce(5)-O7	2.441	2.426
	Ce(1)-O2	2.491	2.489	2 TE	Ce(5)-O4	2.444	2.417
	Ce(1)-O3	2.412	2.392		Ce(5)-O5	2.435	2.413
3 TE	Ce(5)-O1	2.616	2.608		Ce(5)-O6	2.445	2.425
	Ce(5)-O2	2.594	2.573		Ce(5)-O7	2.441	2.425
	Ce(5)-O3	2.658	2.633		Ce(1)-O4	2.401	2.381
	Ce(1)-O1	2.525	2.510		Ce(1)-O5	2.409	2.391
	Ce(1)-O2	2.530	2.517		Ce(1)-O6	2.401	2.387
	Ce(1)-O3	2.512	2.478		Ce(1)-O7	2.599	2.596
	Ce(6)-O1	2.426	2.394	3 TE	Ce(5)-O4	2.437	2.404
	Ce(6)-O2	2.460	2.419		Ce(5)-O5	2.444	2.414
	Ce(6)-O3	2.638	2.609		Ce(5)-O6	2.404	2.384
					Ce(5)-O7	2.434	2.414
					Ce(1)-O4	2.390	2.384
					Ce(1)-O5	2.363	2.357
					Ce(1)-O6	2.389	2.383
					Ce(1)-O7	2.644	2.654
					Ce(6)-O4	2.448	2.418
					Ce(6)-O5	2.426	2.405
					Ce(6)-O6	2.401	2.375
					Ce(6)-O7	2.485	2.471

Table S3: Ce-O bond distances, comparing 4f-core and 4f-valence potentials for different states with different numbers of Ce³⁺ cations. The left side of the table shows Ce-O distances with surface oxygen atoms and the right-side shows Ce-O distances with sub-surface oxygen atoms bonded to the Ce atom identified by the labels described in Figure 1a. All distances are in Angstrom (Å).

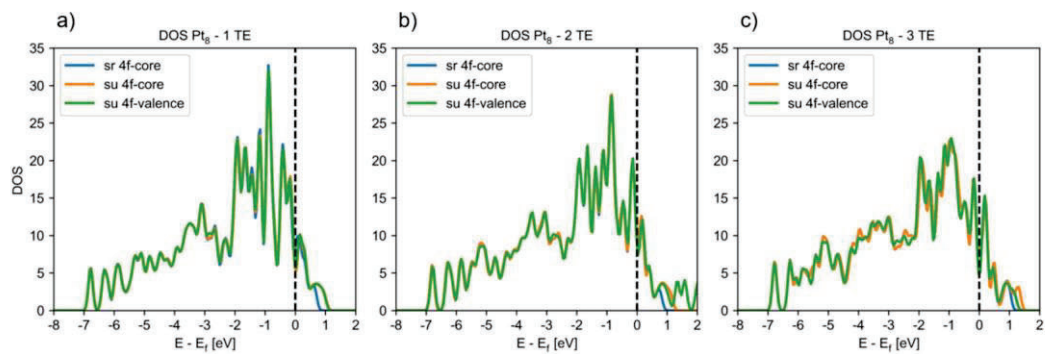


Figure S4: Density of states projected on the Pt atoms of the Pt_8 cluster supported on $\text{CeO}_2(111)$ for the most stable electronic states with a) – one, b) – two and c) - three electrons transferred from the cluster. The methodology to calculate the electronic structure is specified by the color of the lines.

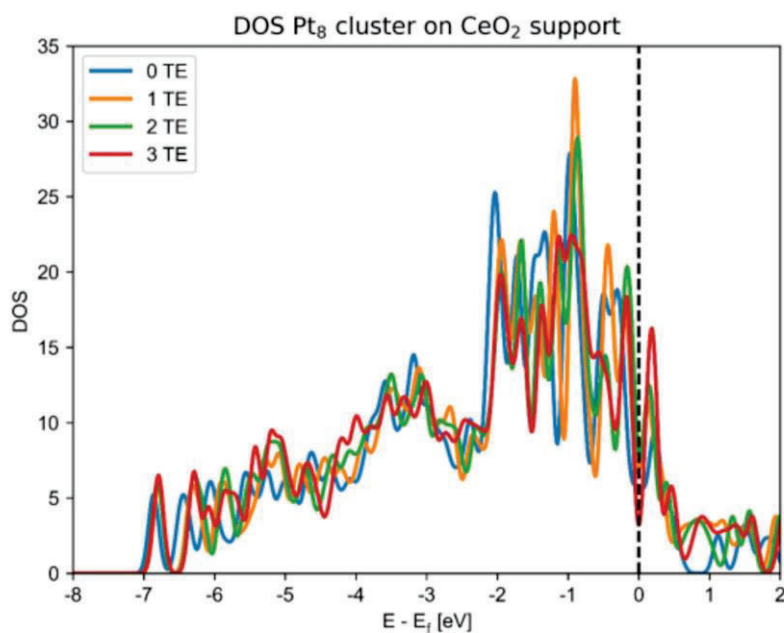


Figure S5: Density of states projected on the Pt atoms of the Pt_8 cluster for 0 to 3 electrons transferred from it, taking the most stable state in each case calculated with the 4f-valence scheme. Energy values are calculated with respect to the Fermi level, marked by a vertical dashed line.

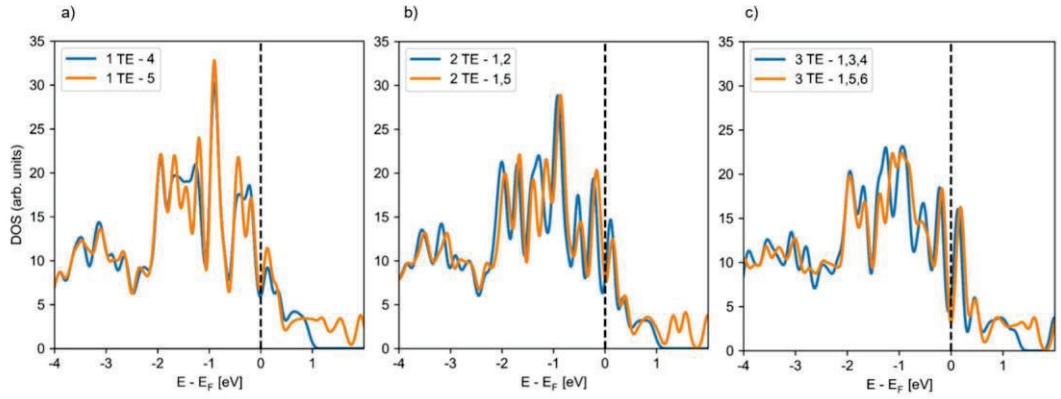


Figure S6: Comparison of total density of states of Pt_8 cluster for different positions of Ce^{3+} cations for 1 to 3 electrons transferred (a, b and c, respectively). The position of Ce^{3+} cations in the legends are depicted in Fig. 1.

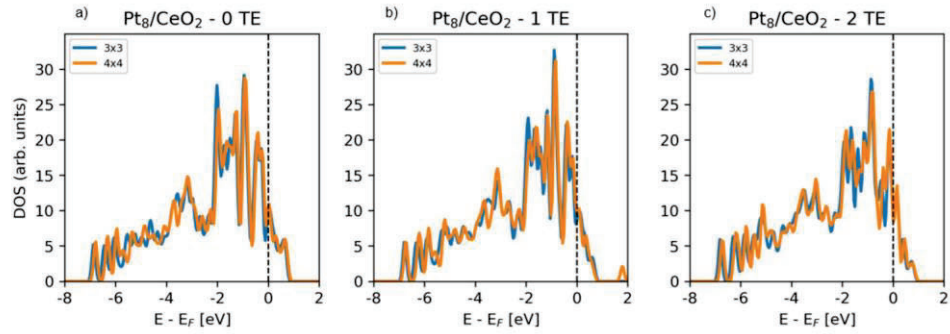


Figure S7: Comparison of total density of states of Pt_8 cluster for different supercell sizes for 0 to 2 transferred electrons (a, b and c, respectively). For 2 TE, the label 1,5 for the 4×4 supercell (Figure S1) was chosen because of its similar chemical environment to the state used for the supported Pt_8 on the 3×3 supercell (Figure 1). The most stable electronic states is evaluated in the 3×3 supercell (with Ce^{3+} in position Ce-5 for 1 TE and Ce-1/Ce-5 for 2 TE). The positions of Ce^{3+} cations in the 4×4 supercell were chosen to be the same with respect to the Pt_8 cluster as in the 3×3 supercell.

System	sp Integral	d Integral	Total Integral
0 TE	6.490	62.264	68.754
1 TE	6.459	62.201	68.66
2 TE	6.583	62.149	68.731
3 TE	6.603	62.043	68.646

Table S4: Integrated total, sp-orbitals and d-orbitals values of density of states (DOS) of the Pt₈ cluster at 0, 1, 2 and 3 transferred electrons.

Number of TE	no TE	1 TE		2 TE		3 TE	
Cluster atom	Ce4f-valence	Ce4f-core	Ce4f-valence	Ce4f-core	Ce4f-valence	Ce4f-core	Ce4f-valence
Pt-1	-0.14	-0.10	-0.11	-0.12	-0.12	-0.13	-0.13
Pt-2	-0.16	-0.14	-0.14	-0.13	-0.13	-0.11	-0.11
Pt-3	0.01	0.04	0.04	0.10	0.10	0.14	0.14
Pt-4	0.01	0.04	0.05	0.10	0.10	0.15	0.15
Pt-5	0.18	0.21	0.21	0.23	0.23	0.25	0.25
Pt-6	0.25	0.27	0.28	0.32	0.32	0.36	0.36
Pt-7	0.20	0.23	0.23	0.22	0.22	0.26	0.26
Pt-8	-0.10	-0.08	-0.07	-0.02	-0.02	0.11	0.11
Total Pt ₈ Charge	0.25	0.47	0.49	0.70	0.70	1.03	1.03

Table S5: Bader charges of Pt atoms in the CeO₂(111)-supported Pt₈ cluster for 0 to 3 transferred electrons. The most stable electronic state is evaluated in each case, comparing values obtained with Ce4f-core and Ce4f-valence potentials. The cluster atoms are labelled as shown in Fig. 1.

Number of TE	1 TE		2 TE		3 TE	
Cluster atom	Ce-5	Ce-4	Ce-1,5	Ce-1,2	Ce-1,5,6	Ce-1,3,4
Pt-1	-0.11	-0.11	-0.12	-0.13	-0.13	-0.1
Pt-2	-0.14	-0.14	-0.13	-0.11	-0.11	-0.14
Pt-3	0.04	0.06	0.1	0.09	0.14	0.12
Pt-4	0.05	0.05	0.1	0.09	0.15	0.13
Pt-5	0.21	0.21	0.23	0.23	0.25	0.26
Pt-6	0.28	0.28	0.32	0.31	0.36	0.34
Pt-7	0.23	0.23	0.22	0.23	0.26	0.24
Pt-8	-0.07	-0.07	-0.02	-0.01	0.11	0.07
Total Pt ₈ Charge	0.49	0.51	0.7	0.7	1.03	0.92

Table S6: Bader charges of Pt atoms in the CeO₂(111)-supported Pt₈ cluster, comparing different positions of Ce³⁺ cations for different number of transferred electrons. The numbers next to Ce indicate the position of formed Ce³⁺ cations and the Pt atoms labelled as indicated in Fig. 1.

Number of TE	0 TE		1 TE		2 TE	
Cluster Atom	3×3	4×4	3×3	4×4	3×3	4×4
Pt-1	-0.14	-0.15	-0.10	-0.13	-0.12	-0.13
Pt-2	-0.16	-0.12	-0.14	-0.12	-0.13	-0.11
Pt-3	0.01	-0.01	0.04	0.03	0.10	0.06
Pt-4	0.01	0.00	0.04	0.02	0.10	0.06
Pt-5	0.18	0.20	0.21	0.21	0.23	0.24
Pt-6	0.25	0.24	0.27	0.27	0.32	0.32
Pt-7	0.20	0.20	0.23	0.22	0.22	0.23
Pt-8	-0.10	-0.10	-0.08	-0.09	-0.02	0.02
Total Pt ₈ Charge	0.25	0.26	0.47	0.42	0.70	0.69

Table S7: Bader charges of Pt atoms in the CeO₂(111)-supported Pt₈ cluster for 0 to 2 transferred electrons on the 4×4 CeO₂ slab. The most stable electronic state is evaluated in the 3×3 supercell, and the positions of Ce³⁺ cations in the 4×4 supercell were chosen to be the same with respect to the Pt₈ cluster as in the 3×3 supercell. All values were obtained using Ce4*f*-core potentials and spin-restricted calculations. The Pt atoms are labelled in Figure S1.

Adsorption site, theory level	0 TE	1 TE		2 TE		3 TE	
		Ce-5	Ce-4	Ce-1,5	Ce-1,2	Ce-1,5,6	Ce-1,3,4
Interface							
Pt-8, 4 <i>f</i> -core-sr	-1.80	-1.91	-1.94	-2.09	-2.10	-2.34	-2.24
Pt-8, 4 <i>f</i> -core-su	-1.78	-1.89		-2.12	-2.14	-2.37	-2.22
Pt-8, 4 <i>f</i> -valence-su	-1.78			-2.02		-2.30	
Second-layer							
Pt-1, 4 <i>f</i> -core-sr	-2.46	-2.40	-2.45	-2.36	-2.43	-2.35	-2.31
Pt-1, 4 <i>f</i> -core-su	-2.43	-2.38	-2.42	-2.37	-2.44	-2.38	-2.30
Pt-1, 4 <i>f</i> -valence-su	-2.43	-2.30		-2.42		-2.34	

Table S8: CO adsorption energies (in eV) on the interface Pt-8 and second-layer Pt-1 sites of Pt₈/CeO₂ for the electronic states with 0 to 3 transferred electrons (TE) from Pt₈, calculated at several levels of theory, including spin-restricted (sr) and spin-unrestricted (su) calculations using the 4*f*-core potential for describing Ce³⁺ cations, and spin-unrestricted calculations using the 4*f*-valence potentials only. Missing values indicate that those states could not be converged to at the corresponding level of theory.

CO Adsorption Energy [eV]		
	3×3	4×4
0 TE	-1.80	-1.75
1 TE	-1.91 (5)	-1.82 (5)
2 TE	-2.09 (1,5)	-2.20 (1,5)

Table S9: CO adsorption energies for different Pt_8 coverages corresponding to the 3×3 and 4×4 supercells. In parentheses are labels of positions of Ce^{3+} ions, see Figures 1 (3×3) and S1 (4×4). All adsorption energies are calculated at 4/core-sr level.

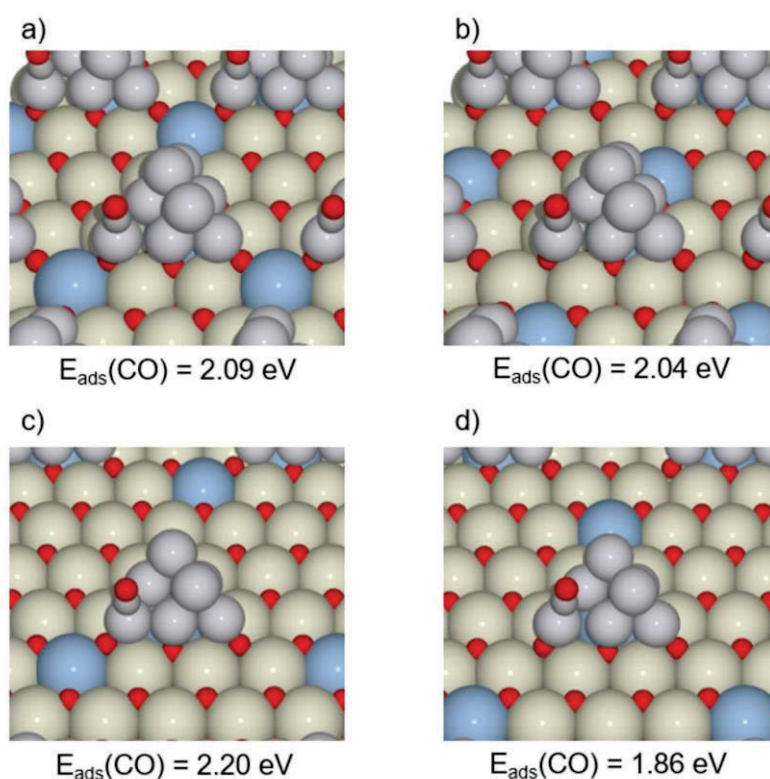


Figure S8: Optimized structures of the $\text{CO}/\text{Pt}_8/\text{CeO}_2(111)$ models, in which CO molecule is adsorbed on the interface site in the 3×3 and 4×4 supercells, and the corresponding CO adsorption energies. a) – label 1,5 and b) – label 2,5 (3×3, Figure 1); c) – label 1,5 and d) – label 5,7 (4×4, Figure S1). Color coding of atoms: Pt – light grey, Ce^{4+} – beige, Ce^{3+} – light blue, O – red, C – dark grey.

Adsorbate	H		H ₂ O		OH		CO	
Adsorption site	Inter-face	Second layer	Inter-face	Second layer	Inter-face	Second layer	Inter-face	Second layer
0 TE	-0.54	-0.79	-0.37	-0.75	-3.45	-4.03	-1.80	-2.46
1 TE	-0.60	-0.73	-0.44	-0.73	-3.48	-3.96	-1.91	-2.45
2 TE	-0.74	-0.70	-0.62	-0.71	-3.65	-3.96	-2.09	-2.43
3 TE	-0.87	-0.68	-0.85	-0.71	-3.76	-4.00	-2.34	-2.31

Table S10: Adsorption energies (in eV) of H, H₂O, OH, and CO adsorbates on the interface Pt-8 and the second-layer Pt-1 adsorptions sites, at 0 to 3 transferred electrons, calculated spin-restricted. The positions of Ce³⁺ cations described by the Ce4f-core potential are Ce-5 for 1 TE, Ce-1,5 for 2 TE, and Ce-1,5,6 for 3 TE.

Chapter 4: Electronic and Structural Properties of FeO/CeO₂ system

4.1 Introduction

Cerium oxide (CeO₂) is a relevant material for different applications such as energy storage or heterogeneous catalyst for reactions like water-gas shift (WGS) reaction,¹ because of its easily removable surface oxygen atoms and the properties of the Ce⁴⁺/Ce³⁺ redox pair.^{1,2} CeO₂ can also be modified by metals in the form of either supported metal particles (giving rise to MSI) or as dopants.^{3,4} Although ceria-supported noble metals have shown excellent catalytic performance,⁵ their high cost limit scaling and wide implementation. This makes the modification of CeO₂ by more abundant and cheaper transition metals (TM) an attractive choice to improve its catalytic performance and cost-effectiveness.⁴

Among the different TM, iron (Fe) has been explored as a promising alternative to modify CeO₂,^{6–11} improving its catalytic performance for reactions such as CO oxidation and NO oxidation.^{12–17} This can be attributed to changes in the morphology with a higher number of active sites, favorable electron transfer between Fe²⁺-Ce⁴⁺ and Fe³⁺-Ce³⁺ sites, enhanced oxygen vacancy formation (and the related oxygen storage capacity) of ceria, and stabilization of more dispersed supported metal particles.¹⁶

Despite evidence of the improved catalytic activity by Fe-modified CeO₂, the nature of the Fe-Ce interaction is still debated. There are contradictory reports about the formation of solid solutions after Fe doping.^{14,18} Other studies focused on the combined redox behavior of Ce (Ce⁴⁺/Ce³⁺) and Fe (Fe²⁺/Fe³⁺) and how this is a consequence of more favorable oxygen vacancy formation,^{7,12,19} while similar studies show absence of Ce³⁺ due to the distribution of Fe³⁺ and decreased oxygen vacancy concentration.¹⁸ It is worth noting that most of these studies are focused on complex powder catalysts, rather than well-ordered model catalysts.

An experimental-computational collaboration was carried out to obtain a better understanding of the catalytic materials formed by combining Fe and CeO₂ interaction, studying model Fe/CeO₂ catalysts by combining spectroscopic, microscopic and computational techniques. The main objective of this chapter is to present computational results obtained from DFT calculations to describe the stability, structural and electronic properties of the FeO_x/CeO₂ oxide-oxide interface.

4.2 Experimental results

The model system prepared experimentally shows many of the surface sites that define the catalytic properties of $\text{FeO}_x\text{-CeO}_2$ systems: $\text{CeO}_2(111)$ facets and step edges, FeO_x 3D clusters, FeO_x 2D layer and the $\text{FeO}_x/\text{CeO}_2$ interface. Importantly, a 2D FeO_x thin film supported on the CeO_2 was observed by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED), as observed in Figure 4.1. STM images reveal a thin film structure, with a constant average height over the CeO_2 support while LEED images show the unit cell of both CeO_2 and FeO and a Moiré superstructure as consequence of the FeO-CeO_2 interface.

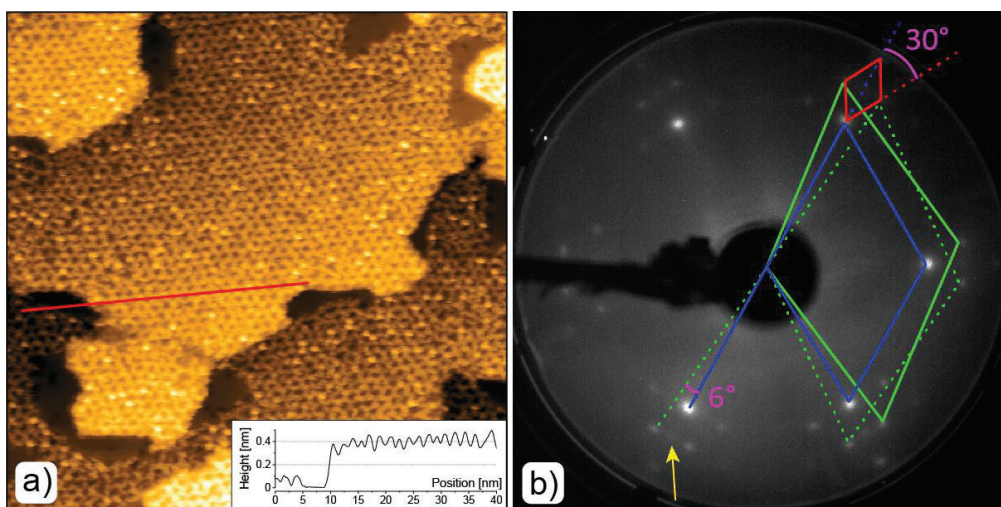


Figure 4.1: Experimental measurements of the structure of the FeO_x thin film supported on CeO_2 . a) STM image. The red line corresponds to a height profile shown in the bottom right plot. b) LEED measurement indicating the symmetry of the unit cells of the $\text{CeO}_2(111)$ surface, the 2D FeO_x layer, and the Moiré superstructure formed (shown by blue, green and red parallelograms, respectively).

The oxidation state of Fe atoms that belong to the FeO_x 2D layer was characterized by X-ray photoelectron spectroscopy (XPS), shown in Figure 4.2. XPS shows a higher proportion of Fe^{3+} over Fe^{2+} in the thin film, but also reveals information about the oxidation states of Fe atoms in the diverse types of nanostructures formed at the CeO_2 surface.

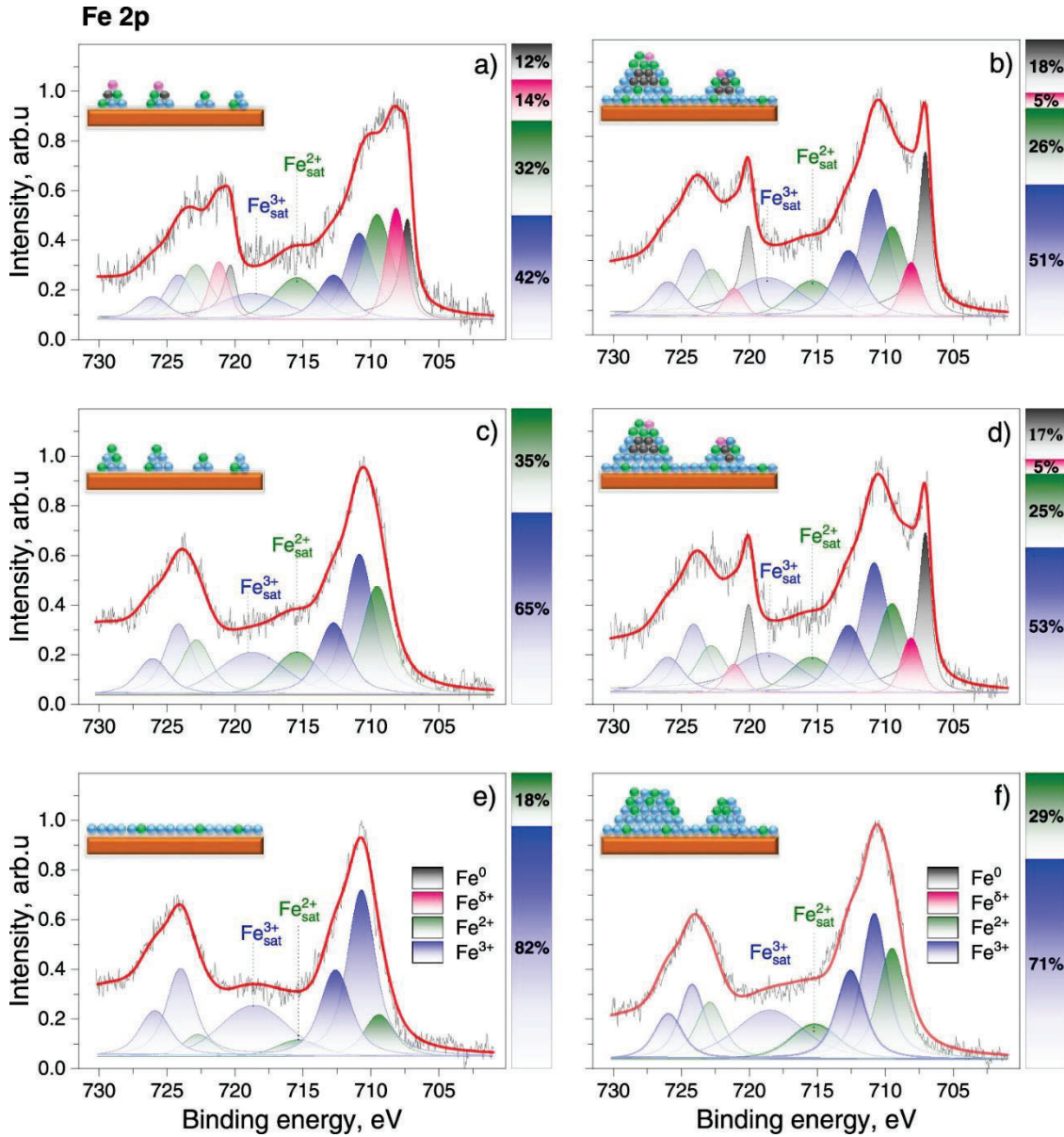


Figure 4.2: XPS Fe 2p core level spectra of FeO_x nanostructures on the CeO₂(111) surface, where a-d) are FeO_x clusters of different sizes, e) is a 2D FeO_x thin film and f) big oxidized FeO_x clusters formed by the same treatment than the 2D FeO_x thin films. Green, blue, pink and grey peaks correspond to the oxidation states of Fe²⁺, Fe³⁺, Fe^{δ+} and Fe⁰ respectively.

4.3 Computational Models

Different structural models were proposed to study the stability, electronic structure, and geometric features of the two-dimensional FeO_x thin films, both exhibiting, as revealed through the experimental techniques, a single layer FeO film with the hexagonal symmetry supported on the CeO₂(111) surface. In particular, we considered a smaller 2×2 supercell of the hexagonal FeO monolayer (ML) supported on a $\sqrt{3} \times \sqrt{3}$ supercell of the CeO₂(111) surface (Figure 4.3a), and a larger 6×6 supercell of the same FeO hexagonal ML supported on a 5×5 supercell of

the CeO_2 (111) surface (Figure 4.3b). These models allow evaluating different properties of the system such as stability with respect to Fe-doped models and 3D FeO_x particles, electron transfer from FeO to CeO_2 , structural features, and reactivity towards further oxidation of the FeO ML.

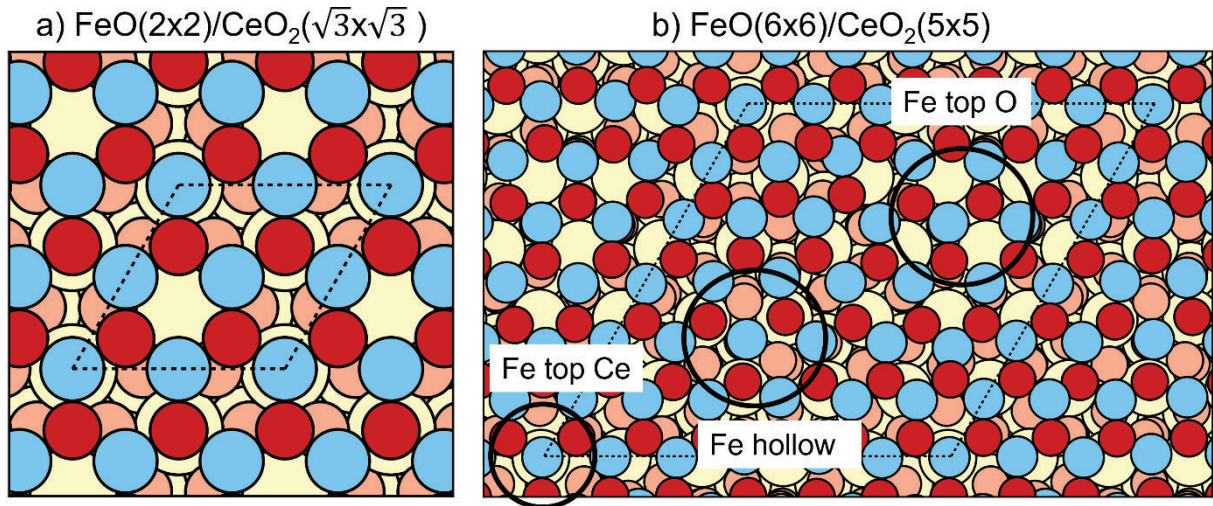


Figure 4.3: Structural models for FeO/ CeO_2 (111) interface. a) $\text{FeO}(2 \times 2)/\text{CeO}(\sqrt{3} \times \sqrt{3})$ and b) $\text{FeO}(6 \times 6)/\text{CeO}_2(5 \times 5)$ supercells respectively. Blue and red circles correspond to Fe and O atoms from the FeO thin film, while beige and orange circles represent Ce and O atoms from the CeO_2 support. In b), regions with different positions of Fe atoms with respect to the CeO_2 support are indicated and the dashed lines denote the supercell boundaries.

Since the optimized lattice parameters of the hexagonal FeO ML and the CeO_2 (111) surface are incommensurate (3.35 and 5.48 Å respectively), it is necessary to apply a some strain (artificial expansion or compression) in one of the components to make both supercells commensurate. To explore the properties of FeO minimizing the biases from the structural design of the models, the lattice parameters of the CeO_2 support were modified. For the $\text{FeO}(2 \times 2)/\text{CeO}(\sqrt{3} \times \sqrt{3})$ model, a compressive strain of 0.16% was applied while for the $\text{FeO}(6 \times 6)/\text{CeO}_2(5 \times 5)$ an expansion of its lattice parameter by 3.63% was necessary to make the FeO and CeO_2 supercells commensurate. For both models, 10 Å of vacuum were considered in the z-axis, while the CeO_2 support consists of three O-Ce-O tri-layers with the bottom tri-layer kept fixed on bulk positions.

As shown in Figure 4.3, the $\text{FeO}(2 \times 2)/\text{CeO}(\sqrt{3} \times \sqrt{3})$ model consists of 4 FeO units supported on 3 CeO_2 surface units. This computationally tractable system size makes feasible the evaluation of different orientations of the FeO ML with respect to the CeO_2 support and of various resulting electronic states. By contrast, the $\text{FeO}(6 \times 6)/\text{CeO}_2(5 \times 5)$ model reproduces

the coexistence of different Fe-CeO₂ positions in the Moiré lattice, but the large size of this system limits the number of evaluated orientations and electronic states.

4.4 Results

Using DFT calculations, the structural of the two different models was locally relaxed, revealing that the interactions between the FeO ML and the CeO₂ support leads to a corrugated FeO structure. The FeO(2×2)/CeO(√3×√3) model shows a corrugation of ~0.7 Å, while the FeO(6×6)/CeO₂(5×5) model shows a corrugation of ~2.3 Å. The height profiles of both models can be seen in Figure 4.4.

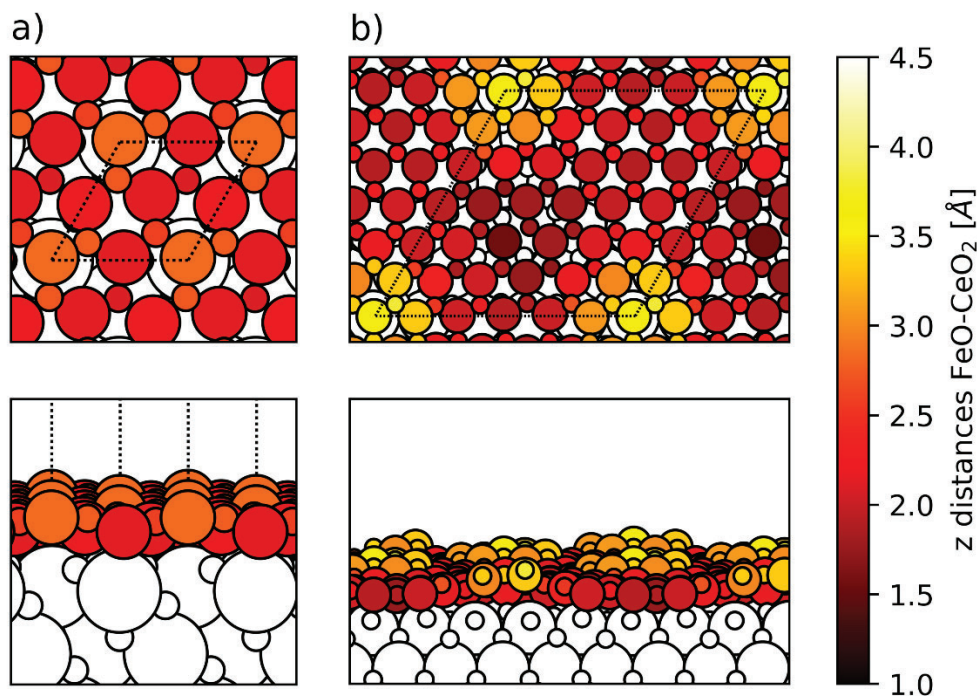


Figure 4.4: Height profile for the a) FeO(2×2)/CeO(√3×√3) and b) FeO(6×6)/CeO₂(5×5) models. Atoms from the CeO₂ support are shown as white circles (small circles are O atoms and big circles are Ce atoms), while the atoms of the FeO thin film are colored according to their z-coordinate with respect to the CeO₂ support, as indicated in the colorbar in the right-hand side. Top and side views for both models are shown.

For the FeO(6×6)/CeO₂(5×5) model, the corrugation leads to the formation of Ce-O_{FeO} and Fe-O_{CeO2} bonds, with bond distances between 2.6 ~ 2.7 Å (close to the 2.43 Å of Ce-O bonds in the clean surface) for the former and between 1.9 ~ 2.2 Å (similar to 1.93 Å on FeO ML) for the latter.

Both models show a very similar adhesion energy (-0.47 eV/FeO unit and -0.45 eV/FeO unit for the FeO(2×2)/CeO(√3×√3) and FeO(6×6)/CeO₂(5×5) model respectively), given by equation Y:

$$E_{\text{adh}} = E(\text{FeO/CeO}_2) - E(\text{FeO}) - E(\text{CeO}_2)$$

Since the energy difference between the freestanding FeO ML and the monoclinic phase of bulk FeO is -0.36 eV, the adhesion energies suggest that forming the oxide-oxide interface is more thermodynamically favorable than forming 3D FeO. It is also important to note the relevant effect of dispersion forces in this system, where up to -0.2 eV of the adhesion energy corresponds to Van der Waals interactions.

An important aspect of the FeO/CeO₂ interface that arose during these calculations is the redox behavior between the FeO ML and the CeO₂ surface – several electronic states are possible where electrons are transferred from Fe²⁺ species to Ce⁴⁺, giving rise to Fe³⁺ and Ce³⁺ centers. The most stable state found for the FeO(6×6)/CeO₂(5×5) model exhibited 6 such transferred electrons, resulting in a 1:5 Fe³⁺/Fe²⁺ ratio and 6 reduced Ce³⁺ centers. The FeO(2×2)/CeO(√3×√3) model allowed for a more systematic evaluation of this phenomenon, showing that states with a 1:3 Fe³⁺/Fe²⁺ ratio are more stable by up to 0.1 eV per FeO unit than states without transferred electrons. The formation of Ce³⁺ cations was evaluated using Ce4f-core potentials, following the same procedure described in Chapter 3. The different electronic states obtained are shown in Figure 4.5.

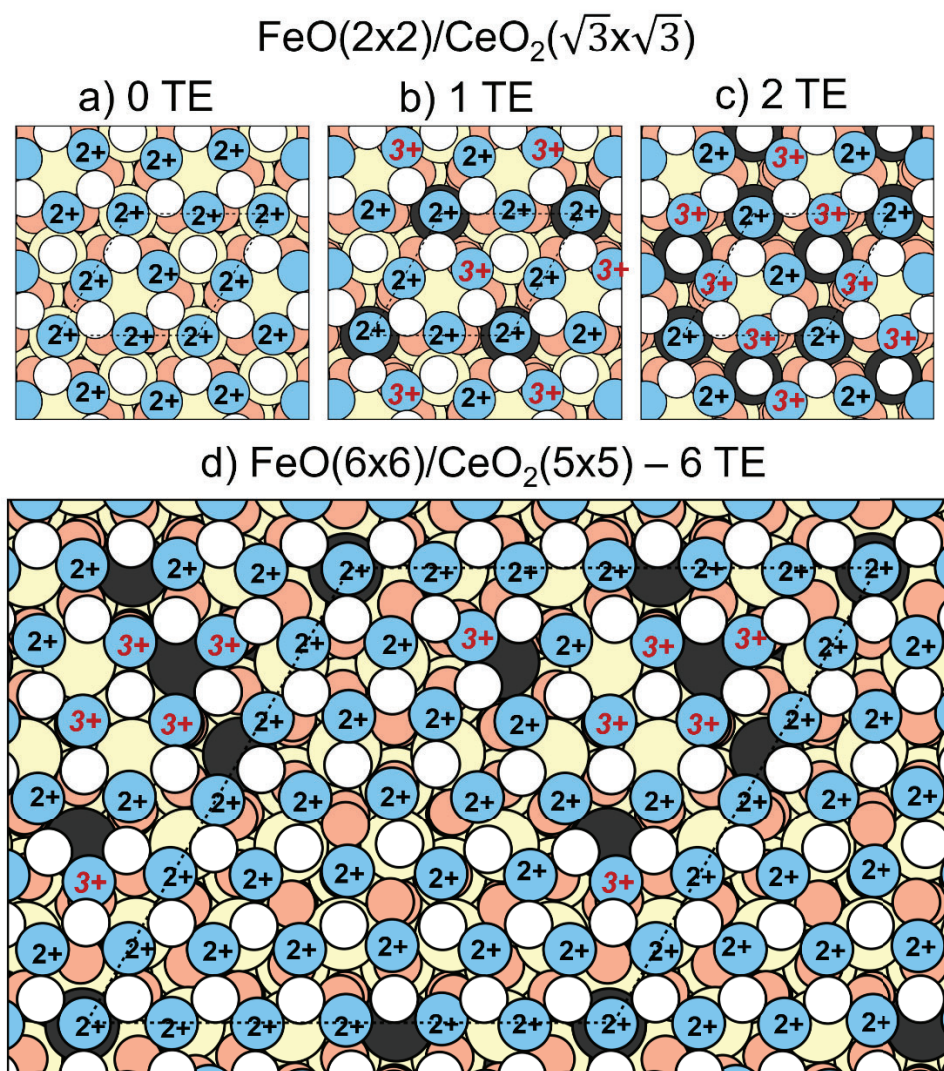


Figure 4.5: Electronic states and formal Fe and Ce atomic oxidation states of systems with different numbers of transferred electrons (TE) for the $\text{FeO}(2 \times 2)/\text{CeO}(\sqrt{3} \times \sqrt{3})$ model (a, b and c) and for the $\text{FeO}(6 \times 6)/\text{CeO}_2(5 \times 5)$ model (d). Blue and white circles are Fe and O atoms from the FeO thin film, while beige, black and orange circles represent Ce^{4+} , Ce^{3+} and O atoms from the CeO_2 support. The labels on the blue circles describe the oxidation state of the corresponding Fe atom (2+ or 3+).

This phenomenon was coined Electronic Oxide Support Interactions (EOSI) and is analogous to the EMSI described in Chapter 3, with the difference being the nature of the supported specie. EOSI can be identified by calculation of Bader charges and by the change in the magnetic moments of Fe atoms. Bader charges of Fe^{2+} are typically $\sim 1.4 |e|$ while for Fe^{3+} they are $\sim 1.8 |e|$. Due to changes in 3d orbital occupation, the magnetic moment of Fe atoms also increases from $\sim 3.7 \mu_B$ to $\sim 4.1 \mu_B$ and correlates with the projected density of states (pDOS) of Fe atoms as seen in Figure 4.6.

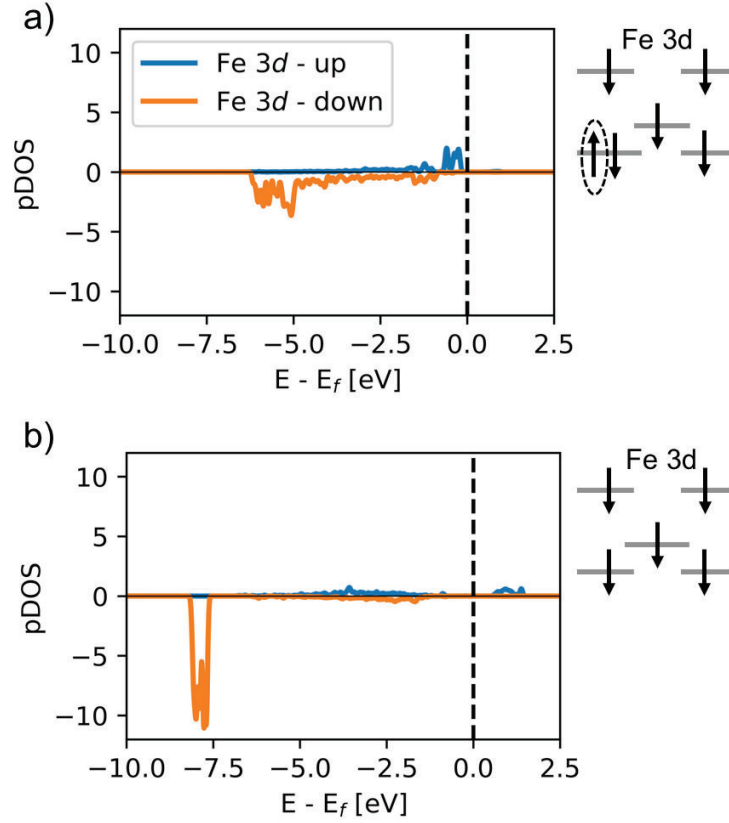


Figure 4.6: Projected Density of States (pDOS) of Fe atoms with oxidation state 2+ (a) and 3+ (b). The electronic configuration of the corresponding Fe atoms is depicted in the right-hand side of the pDOS plots.

The electronic structure of the optimized models agrees partially with the experimental results. Both Fe³⁺ and Fe²⁺ species were revealed by XPS, but with a higher Fe³⁺/Fe²⁺ ratio than in the DFT calculations. The higher 1:5 Fe²⁺/Fe³⁺ experimental ratio suggests that the oxidation of the FeO ML can only be partially attributed to electron transfer to the CeO₂ support and other oxidation mechanisms may be present. To explore this, the stability of states of 2D FeO_x-further oxidized by O adsorption were sampled using the FeO(2×2)/CeO(√3×√3) model, where O were added to evaluate the relative stabilities of Fe₄O₄, Fe₄O₅ and Fe₄O₆ oxidation states as illustrated in Figure 4.7.

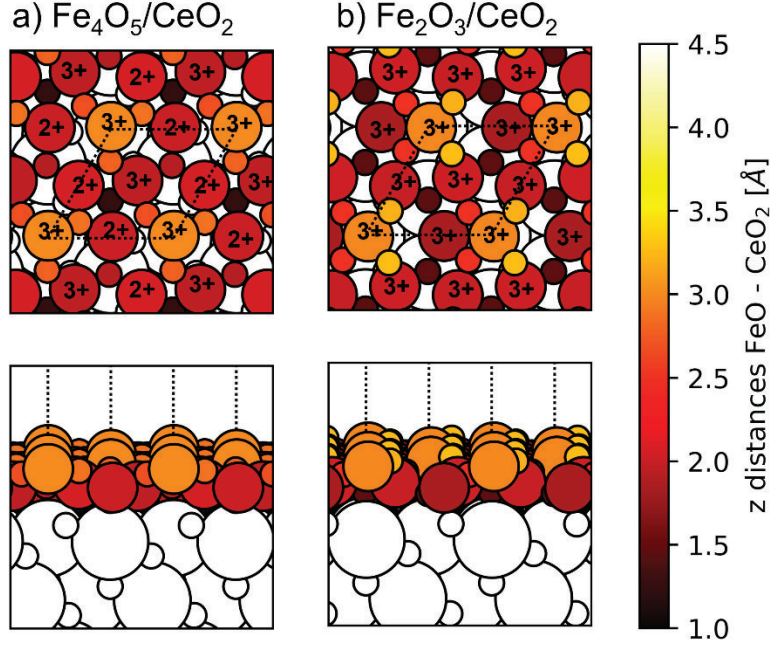
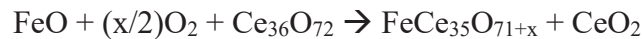


Figure 4.7: Different oxidation states of FeO(2×2)/CeO(√3×√3) model. The change on the oxidation state is due to the adsorption of one (a) or two (b) O atoms on the FeO thin film, resulting in Fe₄O₅ and Fe₄O₆ structures, respectively. Small and big white circles are O and Ce atoms from the CeO₂ support, while colored big circles and small circles are Fe and O from the FeO_x thin film, color coded with respect to their distance to the CeO₂ support (colorbar in the right-hand side).

The results for the Fe₄O₅ state, which exhibits 2 Fe²⁺ and 2 Fe³⁺ cations, indicates that the addition of one O atom to the reoxidizes the only present Ce³⁺ cation to Ce⁴⁺ and one Fe²⁺ to Fe³⁺. Upon adding an additional O atom to form the Fe₄O₆ state, the two remaining Fe²⁺ cations are oxidized to Fe³⁺. The calculated adsorption energies are -0.72 and -1.26 eV for the first and second O atom, respectively. These values indicate a favorable oxidation process on the supported FeO ML by gas-phase O₂.

Fe-doped CeO₂ has been calculated by replacing one Ce atom with an Fe atom on a supercell of CeO₂(2√3×2√3) to compare the stability between the FeO ML with respect to Fe-doped CeO₂ systems (Figure 4.8), which have been described as important structures in catalysts based on Fe and CeO₂ following the reaction:



For this reaction, x takes values of 1, 0 or -1 depending on the oxidation state of the surface, 1 being a fully oxidized surface, 0 with one O vacancy and -1 with 2 O vacancies. FeO corresponds to the monolayer and CeO₂ to bulk ceria. The doping energy can be calculated as:

$$E_{\text{dop}} = E(\text{FeCe}_{35}\text{O}_{71+x}) + E(\text{CeO}_2) - E(\text{FeO}) - E(\text{Ce}_{36}\text{O}_{72}) - (x/2)E(\text{O}_2)$$

The calculated values for E_{dop} are 0.66, 1.09 and 2.66 eV for the system with 0, 1 and 2 vacancies respectively. It can be seen that doping CeO_2 with Fe is an endothermic process, requiring energy while the formation of the FeO ML is an exothermic process which is 1.13 eV more stable than Fe-doped CeO_2 structures.

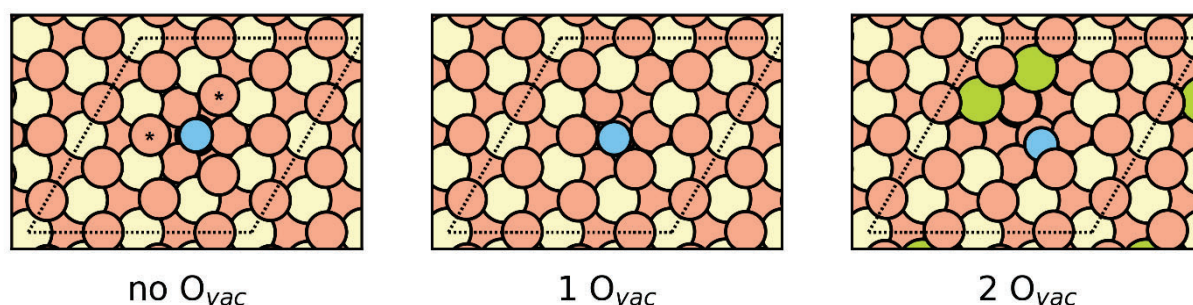


Figure 4.8: Fe-doped structures of fully oxidized and fully reduced $\text{CeO}_2(111)$. Blue, orange, beige and green represent Fe, O, Ce^{4+} and Ce^{3+} , respectively. To form O vacancies, the atoms indicated with asterisk in the left-hand side image are removed.

4.5 Conclusions

Different computational models were constructed to characterize the structure, electronic properties, and chemical reactivity of an experimentally prepared 2D FeO monolayer supported on the CeO_2 (111) surface. FeO_x species were deposited on CeO_2 to synthesize the model catalyst, giving rise to an ordered hexagonal 2D FeO_x thin film, as observed by STM and LEED.

The DFT results indicate that the FeO 2D layer is more thermodynamically stable than bulk FeO or the Fe-doped $\text{CeO}_2(111)$ surface. The stability of the FeO_x monolayer is attributed to dispersion forces in the oxide-oxide interface, to the formation of $\text{Fe-O}_{\text{ceria}}$ and O-Ce bonds, to electron transfer from the FeO thin film to the CeO_2 support, and to further oxidation of the FeO film.

4.6 References

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4.7 Publication

Electronic and Structural Properties of Thin Iron Oxide Films on CeO₂

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ABSTRACT: Modification of CeO₂ (ceria) with 3d transition metals, particularly iron, has been proven to significantly enhance its catalytic efficiency in oxidation or combustion reactions. Although this phenomenon is widely reported, the nature of the iron–ceria interaction responsible for this improvement remains debated. To address this issue, we prepared well-defined model FeO_x/CeO₂(111) catalytic systems and studied their structure and interfacial electronic properties using photoelectron spectroscopy, scanning tunneling microscopy, and low-energy electron diffraction, coupled with density functional theory (DFT) calculations. Our results show that under ultrahigh vacuum conditions, Fe deposition leads to the formation of small FeO_x clusters on the ceria surface. Subsequent annealing results in the growth of large amorphous FeO_x particles and a 2D FeO_x layer. Annealing in an oxygen-rich atmosphere further oxidizes iron up to the Fe³⁺ state and improves the crystallinity of both the 2D layer and the 3D particles. Our DFT calculations indicate that the 2D FeO_x layer interacts strongly with the ceria surface, exhibiting structural corrugations and transferred electrons between Fe²⁺/Fe³⁺ and Ce⁴⁺/Ce³⁺ redox pairs. The novel 2D FeO_x/CeO₂(111) phase may explain the enhancement of the catalytic properties of CeO₂ by iron. Moreover, the corrugated 2D FeO_x layer can serve as a template for the ordered nucleation of other catalytically active metals, in which the redox properties of the 2D FeO_x/CeO₂(111) system are exploited to modulate the charge of the supported metals.

KEYWORDS: ceria, CeO₂, iron oxide, 2D layer, catalysis, STM, XPS, DFT

1. INTRODUCTION

Over the past decade, cerium dioxide (ceria, CeO₂) has remained a leading material for energy storage, electrocatalysis, and heterogeneous catalytic applications.¹ Benefiting from the unique redox potential of the Ce⁴⁺–Ce³⁺ couple and the facile formation of oxygen vacancies (V_O), ceria is able to provide an excellent support for noble metals which are known to exhibit high catalytic performance.² Although noble metal-based catalysts show sufficient activity over a wide range of temperatures, their scale-up implementation is limited by their scarcity and high cost. Therefore, the development of an active and inexpensive catalyst is highly desirable.

Modification of CeO₂ with transition metals (TMs) such as iron aims to enhance its catalytic performance while keeping the price of the resulting catalysts low.³ Recent studies have shown that the addition of iron to ceria significantly improves its performance in CO oxidation, NO oxidation and soot combustion.^{3–5} Morphologically, this can be attributed to an increased specific surface area and a higher number of open active sites.^{4,6} Electronically, it has been suggested that the promotion of Ce-based oxides with Fe species facilitates electron transfer between the mixed Fe²⁺–Ce⁴⁺ and Fe³⁺–Ce³⁺ sites,

which had been identified as active centers in various catalytic processes.^{6,7} Furthermore, iron-modified ceria shows not only improved redox properties but also promotes the dispersion of supported metal nanoparticles and enhances the interaction of metal species with ceria supports.⁸

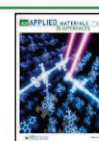
While the improved activity of Fe–Ce mixed oxide catalysts has been widely reported, the nature of the iron–ceria interaction remains controversial. First, many studies have shown that the introduction of redox-active cations into the CeO₂ lattice gives rise to the formation of homogeneous solid solutions.^{8,9} Specifically, the presence of Fe dopant leads to strong structural distortions, resulting in a hematite-like mixed oxide¹⁰ or ceria-like solid solutions⁹ with a higher density of oxygen vacancies at the surface. However, findings presented by

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Polychronopoulou¹¹ and others^{12,13} demonstrate that iron has a poor solubility in the ceria fluorite lattice compared to the rest of binary TM-doped (TM = Cu, Co, Ni, Zn) ceria systems. Second, it has been documented that the doping of low valence cations such as Fe³⁺ and Fe²⁺ in CeO₂ can facilitate the formation of surface oxygen vacancies.^{4,7,14} The increased occurrence of oxygen vacancies in the Ce–Fe mixed oxide system can be attributed to the combined redox behavior of cerium (Ce⁴⁺/Ce³⁺) and iron (Fe³⁺/Fe²⁺) cations.¹⁴ However, Li et al. reported that the distribution of Fe³⁺ over Ce⁴⁺ sites leads to the absence of Ce³⁺ ions and consequently results in a low oxygen vacancy concentration.⁹ The absence of Ce³⁺ ions is also supported by theoretical calculations, which show that Fe adsorption on the stoichiometric CeO₂(111) surface suppresses the formation of oxygen vacancies in the ceria lattice.¹⁵ These findings underscore the necessity for a better understanding of the Fe–CeO₂ interaction.

In contrast to the majority of previous research, which has primarily focused on complex powder catalysts investigating parameters such as iron content¹⁶ and the distribution of iron ions¹⁷ in Fe-doped CeO₂ structures, the present study examines more precisely defined single-crystalline systems. Despite not having exactly the same characteristics as technical catalysts based on combinations of ceria and Fe, our model systems exhibit many of the surface sites defining the catalytic properties of mixed FeO_x–CeO₂ systems: bare CeO₂(111) facets, CeO₂(111) step edges, FeO_x 3D clusters, the FeO_x 2D layer with edges, and the FeO_x–CeO₂ interface. We investigate the electronic and chemical states of these features using synchrotron radiation photoelectron spectroscopy (SRPES), resonant photoelectron spectroscopy (RPES) and conventional X-ray photoelectron spectroscopy (XPS) techniques. We explore the thermally induced morphological and structural changes of FeO_x/CeO₂(111), particularly the formation of a thin FeO_x layer over the ceria surface, through scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) techniques. To complement and further rationalize these experimental methods, we model the FeO_x/CeO₂(111) interface using density functional theory (DFT) calculations, focusing on the structure of the FeO_x thin film and the interaction between Fe²⁺/Fe³⁺ and Ce⁴⁺/Ce³⁺ redox pairs. Building upon our previous work on metal nanoparticles supported by CeO₂(111) thin films,^{18–20} this multimodal approach not only allows us to gain valuable insights into the interactions within the FeO_x–CeO₂ system but also provides a deeper understanding of the structure–property relationship at the nanoscale.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Well-ordered CeO₂(111) thin films were prepared on Cu(111) and Pt(111) single crystals by the physical vapor deposition (PVD) technique. The Cu(111) (MaTecK GmbH, 99.999% purity) and Pt(111) (MaTecK GmbH, 99.99% purity) samples were cleaned by Ar⁺ sputtering at 300 K and annealing (750 and 950 K, respectively) until no traces of carbon or any other contaminants were found in the subsequent XPS analysis. The CeO₂ thin films were grown by PVD of metallic Ce (Goodfellow GmbH, 99.9%) using an electron-beam evaporator (Tetra GmbH) in 5 × 10^{−7} mbar of oxygen at the deposition rate of about 0.1 monolayer (ML)/min, where 1 ML (CeO₂(111)) corresponds to a 0.31 nm thick layer or about 7.9 × 10¹⁴ cm^{−2} of O–Ce–O groups. The substrate temperature during the CeO₂(111) film growth was kept within a range of 523–723 K, depending on the desired density of step edges on the surface.²¹ The temperature was monitored by a K-type thermocouple attached to the

back of the crystal. The thickness of the prepared layer was determined from the attenuation of the Cu 2p_{3/2} peak or the Pt 4f_{7/2} peak and was about 2.5 nm (8 ML of CeO₂(111)). The surface structure of the CeO₂ layer was confirmed by LEED. Fe (Goodfellow GmbH, 99.99%) was deposited by PVD from an electron-beam evaporator from an Fe rod (2 mm in diameter) onto the CeO₂(111) surface. The deposition was carried out either stepwise (in the study of the growth mechanism) or in one deposition step (in the thermal stability study). The sample was grounded during the deposition. The nominal Fe thickness in Fe/CeO₂(111) systems was determined from the attenuation of the Cu 2p_{3/2} signal from the Cu(111) substrate or the Pt 4f_{7/2} signal from the Pt(111) substrate. The thickness varied within the 0.3–2 ML range. Here, 1 ML = 1.72 × 10¹⁵ cm^{−2}, which corresponds to a surface density of Fe atoms in the most stable (110) crystal plane in the Fe bcc crystal. In the case of STM measurements of the CeO₂(111) surface covered exclusively by the 2D FeO layer, the amount of deposited Fe atoms was determined by considering the fraction of the surface covered by the FeO layer and its measured lattice parameter $a_{\text{FeO}} = 0.31$ nm.

2.2. Synchrotron Radiation Photoelectron Spectroscopy. High-resolution SRPES and resonant photoemission spectroscopy (RPES) experiments were carried out at the Materials Science Beamline (MSB) at the Elettra synchrotron light facility in Trieste, Italy. The UHV end-station of MSB with base pressure 2 × 10^{−10} mbar was equipped with a multichannel electron energy analyzer (Specs Phoibos 150), a nonmonochromatized Mg K α X-ray source (1253.6 eV), LEED optics, a sputter gun (Ar⁺), and a gas inlet system for O₂. During the experiment, two electron-beam evaporators for the deposition of Ce and Fe metals were used.

Spectra acquisition utilizing SRPES was performed for the Ce 4d, Fe 3p, C 1s, and O 1s core levels with photon energies of 180 eV (Ce 4d and Fe 3p), 410 eV (C 1s) and 650 eV (O 1s) to keep the electron kinetic energy around 100 eV with a total resolution of about 0.5 eV. RPES analysis was done by collecting the valence band (VB) spectra at 115, 121.4, and 124.8 eV photon energies. Ce³⁺ valence states resonate strongly at a photon energy of 121.4 resulting in a distinctive peak at about 1.4 eV. On the other hand, Ce⁴⁺ valence states reach their maximum at 124.8 eV, with a peak at about 4.0 eV. By subtracting the off-resonant spectra (115 eV) from the resonant spectra, it is possible to determine the features of D(Ce³⁺) and D(Ce⁴⁺) as shown in Supporting Information. The resonant enhancement ratio (RER) which is equal to D(Ce³⁺)/D(Ce⁴⁺) ratio, provides information about reduction state of the surface cerium cations.¹⁸ In addition to collecting the SRPES spectra, XPS spectra of O 1s, Ce 3d, Fe 2p, and Cu 2p_{3/2} core levels were acquired with a total resolution of 1 eV. All spectra were recorded at normal emission (SRPES and RPES) and 20° off normal (XPS). The binding energies in the spectra obtained with synchrotron radiation were calibrated with respect to the Fermi level (E_F) measured on a clean gold foil. All PES data were processed using the KolXPD fitting software and normalized to the incident photon intensity, as determined by a flux monitor. The obtained Fe 3p and Fe 2p spectra were fitted after subtraction of a composite background which consisted of a baseline spectrum acquired before Fe deposition and the Shirley background. The results of XPS Fe 2p spectra fitting for metallic Fe, Fe₂O, FeO and Fe₂O₃ are reported in Table S1.

2.3. Scanning Tunneling Microscopy. STM experiments were performed in a UHV system (base pressure 1 × 10^{−10} mbar) at Charles University, Prague, Czech Republic. The system is equipped with a scanning probe microscope (Specs SPM Aarhus 150 NAP), a photoelectron spectrometer consisting of a hemispherical electron energy analyzer with a 1D line detector (Specs Phoibos 150 1D-DLD) and a monochromatized Al K α X-ray source (μ -FOCUS 600 equipped with XR 50 MF), LEED, and a quadrupole mass spectrometer (Pfeiffer PrismaPlus).

The FeO_x/CeO₂(111) samples were prepared in situ using two e-beam evaporators and examined by multiple methods without breaking the UHV. The chemical composition and thickness of the prepared FeO_x/CeO₂ layers for STM analysis were probed by UHV XPS. STM imaging was performed at 300 K using a combined STM/AFM Specs KolibriSensor.²² The pressure in the STM chamber during the UHV measurements was below 5 × 10^{−10} mbar. The microscope was

operated in the constant current mode with current set points in the 6–15 pA range and sample voltages in the 2–4 V range. Nanonis electronics controlled the scanning process.

2.4. Computational Details. **2.4.1. Computational Methods.** DFT calculations were carried out using the PW91 functional²³ as implemented in the Vienna ab initio simulation package (VASP).^{24–26} The projector augmented wave method (PAW) was used to describe the interaction between fixed core electrons and explicitly described valence electrons. The PAW potentials describe 2s and 2p electrons explicitly for O, 3d and 4s electrons for Fe and 5s, 5p, 6s, 5d and 4f electrons for Ce. All structures were optimized with convergence criteria of 5×10^{-6} eV for total energies and $0.05 \text{ eV } \text{\AA}^{-1}$ for the forces acting on the atoms.

To properly describe electron localization on 3d states of Fe atoms and 4f states of Ce atoms, the GGA + U approach was employed to introduce energy penalties on partial occupations of Fe 3d and Ce 4f spin-orbitals. In line with previous studies, a U value of 5 eV was used for 3d states of Fe²⁷ and 4 eV was used for 4f states of Ce.²⁸ To describe electronic states involving different numbers of electrons transferred to the CeO₂ support, we used the strategy described in our previous work.²⁹

To account for van der Waals interactions when evaluating the stability of the different FeO_x/CeO₂(111) models considered, we have used the D2 correction of Grimme.^{30,31} Since there are no default parameters for the PW91+U approach used here (nor for plain PW91), we have used those parametrized for the similar PBE functional. We used C_6 and R_0 values of $0.7 \text{ J}\cdot\text{nm}^6/\text{mol}$ and $1.342 \text{ \AA}$ for O,³⁰ $10.8 \text{ J}\cdot\text{nm}^6/\text{mol}$ and $1.562 \text{ \AA}$ for Fe,³⁰ and $20.0 \text{ J}\cdot\text{nm}^6/\text{mol}$ and $1.860 \text{ \AA}$ for Ce.^{32,33}

2.4.2. Structural Models. Two different structural models were used to describe the interface between the 2D FeO thin film and the CeO₂(111) support (Figure 1). The inherent mismatch between the

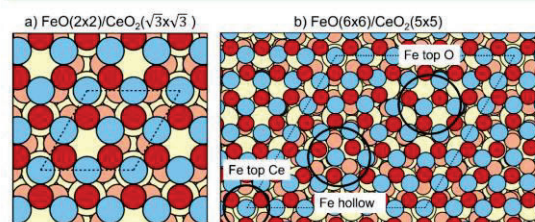


Figure 1. Structural models of the FeO/CeO₂(111) system. FeO(2×2)/CeO₂($\sqrt{3} \times \sqrt{3}$) (a) and FeO(6×6)/CeO₂(5×5) (b) supercells. Blue, red, beige and orange circles correspond to Fe, O atoms in FeO and Ce, O atoms in CeO₂, respectively. Dashed lines indicate the supercell boundaries. In (b), regions with different locations of Fe atoms with respect to the ceria surface are indicated.

2D FeO and CeO₂(111) lattices (with the PW91+U optimized lattice parameters of 3.35 and 5.48 Å, respectively) was solved by combining supercell lattices of FeO and CeO₂(111) of different dimensions and adapting the lattice parameter of the ceria substrate to make commensurate supercell models of the interface. The first, smaller, model corresponds to a 2×2 supercell of the FeO monolayer over a $\sqrt{3} \times \sqrt{3}$ supercell of the CeO₂(111) surface (Figure 1a). This results in a small compressive strain of the ceria surface of just 0.16%. Given the easily tractable size of the supercell (with 4 FeO units and 3 CeO₂ surface units), this model is ideal for systematically evaluating different positions of the FeO ML with respect to the ceria surface (e.g., with a Fe atom located on top of either Ce, O or hollow sites of CeO₂(111)) and different electronic states (i.e., with varying spin orientations and number of electrons transferred from FeO to the ceria substrate). The second, larger, model consists of a 6×6 supercell of FeO on a 5×5 supercell of CeO₂(111) support (Figure 1b). Here, the ceria lattice parameter was stretched by 3.63%. This larger model is a better representation of the experimentally observed supercell and should

better reproduce the coexistence of various Fe–substrate locations and the resulting long-range corrugation. In both models, 10.0 Å of vacuum were included in the z direction, and the CeO₂(111) surface was described by 3 O–Ce–O trilayers, where only the bottom trilayer was kept fixed during structural relaxations.

3. RESULTS

The study is structured into three distinct segments. Initially, we present two sets of SRPES experiments examining the incremental deposition of Fe onto the CeO₂(111) surface at 300 K, as well as the stepwise annealing of the FeO_x/CeO₂(111) surface up to 700 K. These experiments provide valuable insights into the stability of the FeO_x layer and the intricate chemical interactions occurring between the FeO_x and CeO₂ layers. Subsequently, we discuss the structure of the FeO_x layers and their chemical transformations characterized by in situ STM, LEED, and XPS. Finally, the results of the FeO_x/CeO₂(111) DFT calculations are discussed to delve deeper into the observed structures and their associated electronic structures and energetics.

3.1. Deposition of Fe on a Stoichiometric CeO₂(111) Surface.

Figure 2a presents Fe 3p SRPES spectra measured

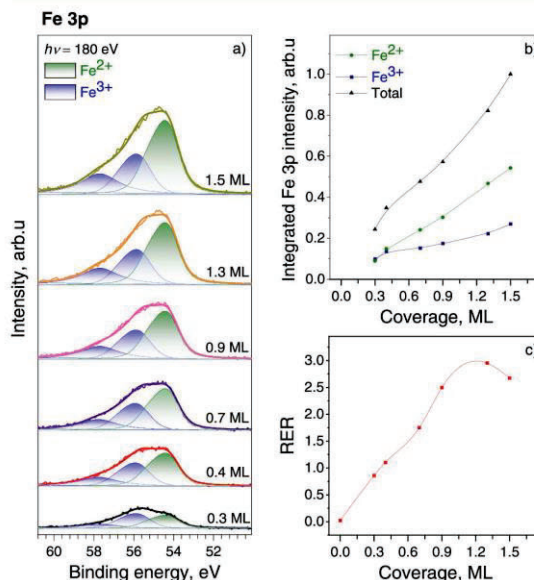


Figure 2. (a) Fe 3p SRPES spectra obtained during stepwise deposition of Fe onto the CeO₂(111) surface at 300 K in UHV; (b) integrated intensities of Fe 3p spectral components; (c) the evolution of the RER shown as a function of Fe coverage.

during stepwise Fe deposition on the CeO₂(111) surface at 300 K in UHV (pressure $\sim 1 \times 10^{-9}$ mbar). The obtained spectra were fitted with two unresolved doublets with a spin–orbital splitting of less than 1 eV. According to the literature, the doublet with the main peak position at about 55.7 eV and additional peak arising due to multiplet splitting at about 58 eV can be attributed to the formation of Fe³⁺ states.^{34,35} The doublet with the main peak at about 54.2 eV originates from the Fe²⁺ species.^{34,35} As can be seen from Figure 2b, both states gradually grew upon increasing the amount of Fe. In the case of 0.3–0.4 ML Fe/CeO₂ surfaces, the concentrations of Fe²⁺ and

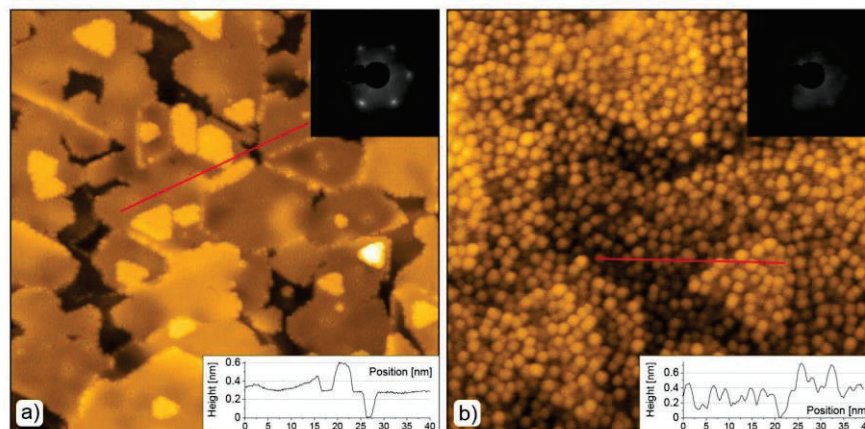


Figure 3. STM images of the clean CeO₂(111) surface (a) and as-deposited 0.7 ML Fe/CeO₂ surface (b). Parameters of the STM images: 80 × 80 nm², $U_s = 3.5$ V, $I_t \approx 10$ pA. LEED patterns of the CeO₂(111) surface without/with Fe taken with a beam energy of 60 eV are shown in the top right insets. Red lines mark the positions of the height profiles shown in the bottom right insets.

Fe³⁺ were similar, whereas starting from the 0.4 ML coverage, Fe²⁺ states became dominant.

The corresponding Fe 2p core level spectra obtained by conventional XPS (Figure S1) also confirmed the formation of Fe²⁺ and Fe³⁺ cations. Since it is not easy to use the peak position of Fe 2p_{3/2} alone to distinguish between different oxidation states of Fe, they are usually detected from satellite features.³⁶ In particular, FeO, consisting of Fe²⁺ ions, typically contains a prominent satellite feature at around ~715 eV (6 eV above the main peak),³⁷ while the broad satellite centered at ~718 eV (8 eV above the main peak) is a characteristic of the Fe³⁺ state.³⁶ During the stepwise deposition of Fe, the Fe 2p spectra revealed a minor satellite at approximately ~718 eV and a progressively increasing peak at around 715 eV.³⁸ These spectral features indicate a successive growth of Fe²⁺ and Fe³⁺ ion content on the CeO₂ surface with each Fe deposition step. From the steeper growth of the Fe²⁺ peak, it can be concluded that Fe³⁺ is likely to be accommodated at the ceria interface while Fe²⁺ ions are formed in the upper layers. The formation of Fe^{2+,3+} states has been reported for Fe submonolayers on Al₂O₃,³⁹ TiO₂,⁴⁰ and ZnO⁴¹ supports, as well as for Fe single atoms on CeO₂⁴² nanoparticles. These observations are also consistent with the general picture of the behavior of metals on oxide supports.⁴³

Deposition of Fe onto the stoichiometric CeO₂(111) surface at 300 K caused an immediate reduction of Ce⁴⁺ ions. The facile conversion of Ce⁴⁺ into Ce³⁺ is evident from the RER displayed in Figure 2c (for the corresponding VB spectra see Figure S2). Before the deposition of Fe, the RER was approximately 0.02, indicating the presence of a negligible amount of Ce³⁺ cations due to intrinsic defects in the surface region of the well-ordered CeO₂(111) film.⁴⁴ At the lowest Fe coverage (0.3 ML), the Ce³⁺ state started to appear and grew slowly with each addition of iron. Up to 1 ML coverage, iron uniformly reduced the ceria surface, increasing the contribution of Ce³⁺ steeply up to the value of 2.95. After exceeding the Fe coverage of 1.3 ML, the RER started to decrease, indicating that the Ce³⁺ content has reached saturation. The observed reduction of Ce⁴⁺ on the ceria surface can be explained by the charge transfer from the iron clusters to the ceria substrate¹⁵ and the migration of O atoms from the ceria surface to the supported Fe clusters. The charge transfer and concomitant reduction of Ce⁴⁺ to Ce³⁺ occurs via

the formation of Fe–O bonds, created at the interface between the FeO_x clusters and the ceria surface and as a result of the O migration (reverse spillover) from the ceria surface to the FeO_x clusters.⁴² This reverse spillover, which involves the formation of O vacancies and has been observed for other ceria-supported metal particles,⁴⁵ is the only mechanism that can explain the oxidation of noninterface Fe²⁺ and Fe³⁺ cations, which would repel each other in the absence of Fe–O–Fe motifs. Once all the surface oxygen is covered with a layer of FeO_x or the ceria surface is saturated with O vacancies, further charge transfer is hindered.

To observe the surface morphology, a 0.7 ML Fe/CeO₂(111) surface was characterized by STM. Figure 3a,b shows STM images obtained from the clean CeO₂(111) and Fe/CeO₂(111) surfaces, respectively. The thin film of CeO₂(111) exhibited a well-ordered structure with a continuous layer terminated by atomically flat terraces, in agreement with our previous studies.²¹ The LEED pattern obtained from this film confirmed its crystallinity. After about 0.7 ML of Fe was deposited on the surface at 300 K in UHV, small circular islands appeared (Figure 3b). These islands were from about 0.2 nm up to 0.6 nm in height, up to 3 nm in diameter and were uniformly distributed across the surface. LEED observation shows almost complete disappearance of the diffraction spots, indicating that the ceria surface was covered by a disordered layer of clusters. These circular entities were interpreted as nonstoichiometric FeO_x clusters by PES. The formation and random distribution of the FeO_x clusters indicates that Fe does not preferentially agglomerate at ceria steps. This is further supported by our experiments with a lower 0.2 ML coverage of FeO_x (see Figure S6). This behavior can be attributed to the high oxophilicity of iron atoms.^{46,47} Due to their high affinity for oxygen and presumably low mobility at 300 K, Fe atoms most likely tend to localize on O sites on the stoichiometric CeO₂(111) terraces, where they experience high diffusion barriers.⁴⁷ Therefore, their growth is dominated by the formation of irregular nanoparticles over the entire surface of the substrate rather than the preferential nucleation on the surface defects.

3.2. Oriented FeO Layer Formation on CeO₂(111). In the next step, the 0.7 ML Fe/CeO₂(111) system was stepwisely annealed in UHV (pressure $\sim 1 \times 10^{-9}$ mbar) up to 700 K. The evolution of the Fe 3p spectra is shown in Figure 4a. We noted

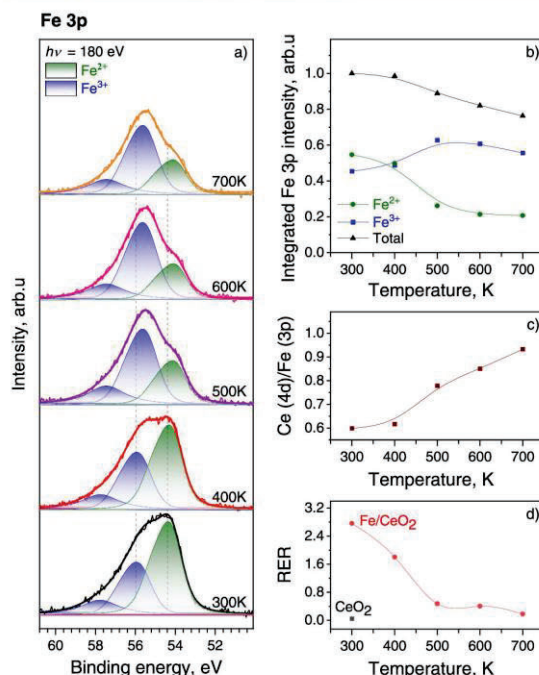


Figure 4. (a) Fe 3p SRPES spectra acquired from the 0.7 ML of Fe on the CeO₂(111)/Cu(111) system in UHV at different temperatures; (b) integrated intensities of the Fe 3p spectral components, (c) Ce/Fe surface atomic ratio and (d) RER as a function of temperature.

that the total spectral intensity within the Fe 3p region remained relatively stable up to 400 K. However, a gradual decrease becomes evident as temperature increases above this point (Figure 4b). An analysis of the Ce/Fe ratio, derived from the Ce 4d and Fe 3p spectral areas divided by corresponding photoionization cross sections as a function of annealing temperature, also revealed a significant decrease in the intensity of the iron signal compared to cerium. These observations strongly suggest changes in the morphology of the deposited iron. As shown in STM images with a higher surface coverage (1–2 ML) in Figure 5, this is partially due to the formation of large FeO_x particles on the surface. Specifically, the growth of these larger FeO_x clusters is expected to expose a greater portion of the substrate, thereby contributing to the increase in the Ce/Fe ratio, as shown in Figure 4c. In addition to the surface changes of the FeO_x layer, this ratio can also be increased by thermally induced diffusion of Fe ions into the bulk of ceria.¹² Furthermore, the elevated temperature promoted the oxidation of Fe ions to a higher valence state. The calculated relative intensities of Fe²⁺ and Fe³⁺ components presented in Figure 4b show that the dominant Fe²⁺ contribution began to drop already at 400 K, and upon reaching a temperature of 700 K, its intensity decreased more than 2-fold in favor of the Fe³⁺ state.

Simultaneously with the oxidation of Fe, a gradual decrease in the amount of Ce³⁺ ions was observed (Figures 4d and S3). The fact that the spectral signal for Fe³⁺ and Ce⁴⁺ states increased during UHV annealing can be explained by the oxygen diffusion from deeper ceria layers to the surface, typically observed within the temperature range of 470–600 K.⁴⁸ This diffusion process together with direct adsorption of oxygen from a residual

atmosphere led to the replenishment of surface oxygen vacancies, which had initially formed due to the Fe–CeO₂ interaction, and to further oxidation of iron.⁴⁹ The accumulation of additional oxygen on the surface, leading to the change in the surface potential, can also explain an observed slight shift of the Fe 3p spectral components to a lower binding energy.

The STM images obtained after annealing of ~1 ML of Fe on the CeO₂(111) surface at 400 and 600 K in UHV (pressure ~1 × 10^{−9} mbar) are shown in Figure 5a,b, respectively. Upon annealing at 400 K, the size and distribution of FeO_x clusters did not change significantly from the ones observed in Figure 3b. However, at 600 K, STM images revealed the appearance of significantly larger FeO_x particles up to 1.5 nm in height and up to 8 nm in apparent lateral size. Additionally, a hexagonal structure covering the rest of the ceria surface emerged. Based on its orientation and visible parameters of the lattice, the structure was interpreted as a moiré pattern, which in STM images arises as a result of electronic or morphological interference between two crystal lattices with the same symmetry but different periodicity.^{50,51} In this case, we observe the overlap of an oriented 2D FeO_x layer and the CeO₂(111) substrate. To the best of our knowledge, the growth of the thin FeO_x layer on the CeO₂(111) substrate has not been reported to date. Nonetheless, the amount of oriented iron oxide is relatively low when the Fe/CeO₂(111) system undergoes annealing in UHV. This is attributed to a substantial portion of iron being incorporated into large amorphous particles, resulting in the above-mentioned lowering of the Fe 3p SRPES signal.

To enhance the formation of the 2D oriented iron oxide overlayer and simultaneously investigate its correlation with the presence of FeO_x particles, we deposited 2 ML of Fe onto the CeO₂(111) substrate at 600 K in 1 × 10^{−8} mbar of O₂. The resulting surface topography can be seen in Figure 5c. Under these conditions, the formation of round FeO_x clusters with heights up to 4 nm and apparent lateral sizes up to 20 nm was observed. The rest of the ceria surface was uniformly covered by the 2D FeO_x layer, the arrangement of which was substantially improved by elevated oxygen pressure. The deposited layer contains a relatively low number of defects, concentrated mostly in the vicinity of CeO₂ and FeO_x step edges. After prolonged annealing in O₂ (Figure 5d), the clusters transition from round hemispherical shapes to faceted pyramidal structures, indicating a structural shift from amorphous to crystalline. In contrast to the striking oxidation-induced morphological changes of the large FeO_x clusters, the 2D layer remains unchanged. This indicates that the 2D FeO_x layer is formed relatively quickly after the deposition at 600 K, while remaining Fe atoms can diffuse more freely on the FeO_x-passivated surface and agglomerate into large clusters.

To further study the structure of the 2D FeO_x layer, unaffected by the amorphous FeO_x clusters, we deposited 0.7 ML of Fe onto the CeO₂ at 300 K in UHV and annealed the sample at 700 K in 1 × 10^{−8} mbar of O₂. This procedure resulted in the surface being completely covered by the moiré superstructure with a relatively high degree of order (Figure 6a), enabling us to determine the structure of the FeO_x layer. Specifically, having calibrated the STM data by the uncovered CeO₂ patches (Figure 6c,d), we determined that the elementary moiré cell is rotated by approximately 30° with respect to the CeO₂ lattice and has a periodicity almost four times greater than the CeO₂ lattice. Based on the lattice constants and the relative orientation of the FeO_x layer, it can be determined that the FeO_x unit cell is rotated by ±6° with respect to the CeO₂ unit cell and

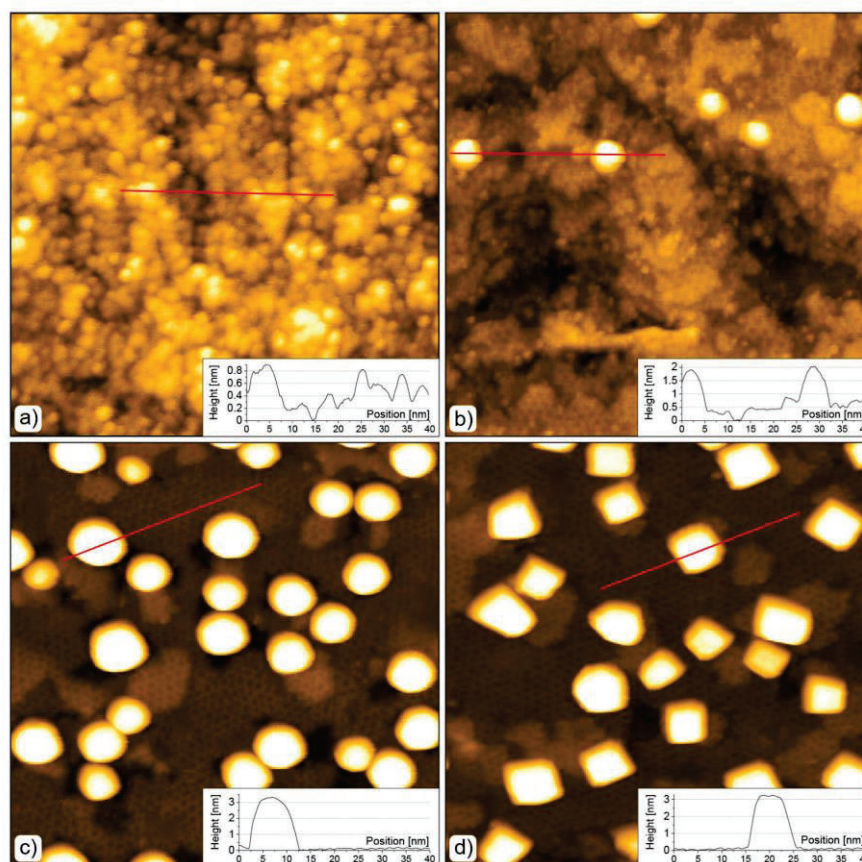


Figure 5. STM images of the $\text{CeO}_2(111)$ surface upon deposition of Fe and subsequent annealing in UHV and oxygen. Top: ~ 1 ML of Fe was deposited on the $\text{CeO}_2(111)$ surface at 300 K and annealed at 400 K (a), and 600 K (b) in UHV. Bottom: 2 ML of Fe was deposited on the $\text{CeO}_2(111)$ surface at 600 K in 1×10^{-8} mbar of O_2 (c) and annealed at 600 K for 20 min in 1×10^{-8} mbar of O_2 (d). All images have the size of $80 \times 80 \text{ nm}^2$ and were obtained with $U_{\text{bias}} \approx 3 \text{ V}$ and $I_t \approx 10 \text{ pA}$. Red lines mark positions of the height profiles shown in bottom right insets.

that the lattice constant of the FeO_x layer is $a_{\text{FeO}_x}^{(111)} = (0.31 \pm 0.01) \text{ nm}$. The atomic periodicity of 0.31 nm corresponds to those obtained for $\text{FeO}/\text{Pt}(111)$ (0.311 nm)⁵⁰ and $\text{FeO}/\text{Ru}(0001)$ (0.308 nm)⁵² and is only slightly higher than that expected from the theoretical calculations of FeO .⁵³

The validity of the measured FeO lattice parameters was also corroborated by the LEED analysis (Figure 6b). Bright, hexagonally arranged spots, marked by a blue parallelogram, correspond to the $\text{CeO}_2(111)-(1 \times 1)$ structure.²¹ Satellite diffraction peaks observed in the vicinity of the main ceria diffraction spots arose due to the superposition of the two metal-oxide lattices and multiple elastic scattering of diffracting electrons on both gratings,⁵⁴ resembling the superstructures reported for $\text{FeO}(111)/\text{Pt}(111)$ and $\text{FeO}(111)/\text{Au}(111)$ surfaces.^{50,55} By comparing the distances of the diffraction spots from the zeroth series with the distances of the (1×1) spots of the CeO_2 substrate, we obtained the lattice constants of the deposited layer (see green parallelograms) and the moiré superstructure (see a red parallelogram) to be $a_{\text{FeO}_x}^{(111)} = (0.31 \pm 0.01) \text{ nm}$ and $a_{\text{moiré}} = (1.55 \pm 0.04) \text{ nm}$, respectively. Furthermore, the angle between the moiré superstructure and

the CeO_2 lattice was determined to be $(30 \pm 1)^\circ$, corresponding to the $(6 \pm 1)^\circ$ angle between the main direction of the (1×1) structure and the FeO structure.⁵⁴ Both of these values agree very well with the values measured from the STM images further indicating that the 2D FeO -like phase is indeed formed on the surface of CeO_2 . Additionally, the presented LEED image features an extra set of spots marked by a yellow arrow. These spots are located in the main crystallographic directions of the $\text{CeO}_2(111)-(1 \times 1)$ structure but correspond to the lattice constant of about 0.31 nm. We assign these spots to a minority FeO -like structure which is aligned with the ceria substrate. The substrate-aligned minority superstructures were also observed in our STM images (see Figure S4).

The structural properties of the $\text{FeO}/\text{CeO}_2(111)$ interface were further elucidated by means of the DFT+U calculations described in the computational details section. For the smaller $\text{FeO}(2 \times 2)/\text{CeO}_2(\sqrt{3} \times \sqrt{3})$ structural model (Figure 1a), we have evaluated three different orientations of the FeO ML corresponding to one of the 4 Fe atoms of the FeO supercell placed on top of an O atom, a Ce atom, or a hollow site of the ceria substrate, respectively. We note that these alternative arrangements involve different interactions between the O_{FeO}

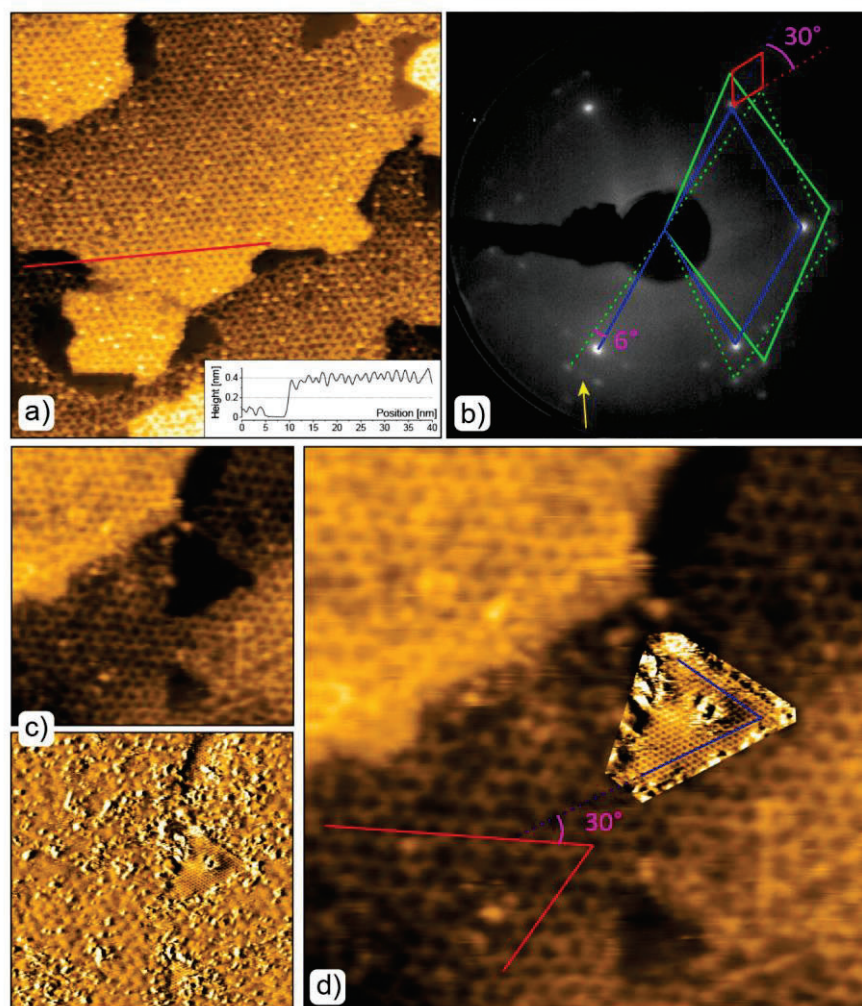


Figure 6. Structure of the 2D FeO_x layer. (a) STM image of the moiré superstructure on the $\text{FeO}_x/\text{CeO}_2(111)$ surface after annealing at 700 K in 1×10^{-8} mbar of O_2 . Surface area $70 \times 70 \text{ nm}^2$, $U_{\text{bias}} \approx 3 \text{ V}$, $I_t \approx 10 \text{ pA}$. (b) LEED image obtained from the same surface. Electron energy: 50 eV. The $\text{CeO}_2(111)$, FeO_x and the moiré superstructure elementary cells are marked by blue, green and red parallelograms, respectively. A diffraction spot corresponding to a minority surface structure with the FeO_x structure aligned with the main direction of $\text{CeO}_2(111)$ is marked by a yellow arrow. (c) Two simultaneously captured STM images showing the structure of the CeO_2 lattice and the moiré superstructure on the FeO_x layer. The top image represents the height channel of the constant current STM image, covering a surface area of $30 \times 30 \text{ nm}^2$, with U_{bias} set at 1.6 V and $I_t \approx 10 \text{ pA}$. The bottom image displays the frequency shift channel as measured by a Kolibri sensor.²² (d) A composite image comprising parts of (c) illustrating the relative orientation of the two structures. Blue and red lines mark the main directions of the ceria and the superstructure lattices, respectively. Relative angles between the structures are marked in (b) and (d).

and the ceria surface, which also affects the overall stability of each structure. The most stable structure found for this model is illustrated in Figures 1a and 7a, exhibiting both an Fe atom and an O_{FeO} atom on top of two different Ce atoms of the ceria surface. The different interactions of Fe and O atoms with the ceria surface lead to a corrugation of $\sim 0.7 \text{ \AA}$, with the Fe and O_{FeO} atoms found at a 3.51 and 2.84 $\text{\AA}$ distance above the underlying Ce atoms, respectively. The calculated adhesion energy E_{adh} between the FeO monolayer and the ceria surface is -0.47 eV per FeO unit (calculated as $E_{\text{adh}} = E(\text{FeO}/\text{CeO}_2) - E(\text{FeO}) - E(\text{CeO}_2)$). This energy gain is larger than the -0.36 eV energy difference between 2D FeO and the most stable

(monoclinic/halite) phase of bulk FeO, which indicates that formation of the FeO/CeO_2 heterostructure is more thermodynamically favorable than agglomerated 3D particles of FeO. A large fraction (-0.20 eV) of this adhesion energy (-0.47 eV) corresponds to van der Waals interactions.

The optimized structure of the larger $\text{FeO}(6 \times 6)/\text{CeO}_2(5 \times 5)$ model is illustrated in Figure 7b and exhibits a more substantial corrugation of $\sim 2.3 \text{ \AA}$. The lowest-lying region of the FeO ML corresponds to that with Fe atoms bonding to O atoms of the ceria surface, with $\text{Fe}-\text{O}_{\text{CeO}_2}$ distances of $\sim 1.9\text{--}2.2 \text{ \AA}$ (similar to the 1.93 $\text{\AA}$ $\text{Fe}-\text{O}$ distances in the free-standing FeO ML). These bonds are formed for several Fe atoms near top

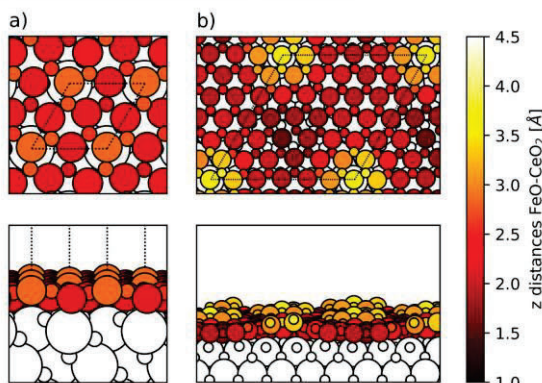


Figure 7. Height profile of the FeO monolayer supported on CeO₂ for the (a) FeO(2 × 2)/CeO₂(√3 × √3) and (b) FeO(6 × 6)/CeO₂(5 × 5) models. Upper and lower panels correspond to top and side views, respectively. The Fe (big circles) and O (small circles) atoms of the FeO monolayer are colored depending on their distance to the CeO₂ support according to the color bar. Distances are calculated with respect to the outermost O atoms of the bare CeO₂(111) surface. The white circles indicate Ce (big circles) and O (small circles) atoms of the CeO₂ surface.

positions of O_{CeO₂} atoms and for one Fe atom on the hollow site between 3 O_{CeO₂} atoms. In the middle-lying region, the O_{FeO} atoms neighboring the Fe atom are also close to Ce atoms of the ceria surface, forming O_{FeO}–Ce bond distances between 2.6 to 2.7 Å, close to those of the Ce–O bonds in the clean ceria surface (2.43 Å). These Fe–O_{CeO₂} and O_{FeO}–Ce distances reflect a strong interaction between the FeO ML and the ceria surface. Indeed, for the FeO(6 × 6)/CeO₂(5 × 5) model, E_{adh} is of −0.45 eV per FeO unit, further confirming the high stability of the FeO/CeO₂ interface. The highest-lying regions of the FeO ML correspond, in turn, to Fe atoms on top of Ce atoms of the ceria surface, with Fe–Ce distances of 4.34 Å. Thus, an apparent repulsion between Fe and Ce cations emerges from both FeO(6 × 6)/CeO₂(5 × 5) and FeO(2 × 2)/CeO₂(√3 × √3) models, although the larger supercell can accommodate more pronounced corrugations leading to significantly longer Fe–Ce distances.

We also compare the stability of the FeO/CeO₂(111) system to that of Fe-doped CeO₂(111), which has been proposed as a relevant component for catalysts based on Fe and CeO₂.^{4,6} To do so, we compare the adhesion energy of FeO to CeO₂(111) to the energy of the Fe-doping reaction using the same 2D FeO reference and a 2 × 2 supercell of the CeO₂(√3 × √3) surface: $\text{FeO} + (x/2)\text{O}_2 + \text{Ce}_{36}\text{O}_{72} \rightarrow \text{FeCe}_{35}\text{O}_{71+x} + \text{CeO}_2$, where $\text{FeCe}_{35}\text{O}_{71+x}$ corresponds to the Fe-doped CeO₂(2√3 × 2√3) surface (see Figure S7) and x takes values of 1, 0, or −1 for the Fe-doped surface when fully oxidized, with one O vacancy, or with two O vacancies, respectively. FeO corresponds to the 2D FeO monolayer, CeO₂ corresponds to bulk ceria, and Ce₃₆O₇₂ is the slab model of the CeO₂(2√3 × 2√3) supercell. E_{dop} is thus calculated as $E_{\text{dop}} = E(\text{FeCe}_{35}\text{O}_{71+x}) + E(\text{CeO}_2) - E(\text{FeO}) - E(\text{Ce}_{36}\text{O}_{72}) - (x/2)E(\text{O}_2)$. The calculated E_{dop} values are 0.66, 1.09, and 2.66 eV per Fe atom, for the Fe-doped CeO₂(111) system with zero, one, and two vacancies, respectively. Considering the calculated E_{adh} (−0.47 eV), the ceria supported FeO monolayer is at least 1.13 eV more stable than Fe-doped

CeO₂(111), which explains why Fe dissolution into the ceria lattice is very limited.

The STM and LEED investigation was also accompanied by in situ XPS measurements aiming to study the surface chemistry of the resulting FeO_x/CeO₂ systems. Two notable sets of Fe 2p spectra are presented in Figure 8 and corresponding Ce 3d spectra in Figure S5. The top-left spectrum in Figure 8 corresponds to the surface covered by relatively small FeO_x clusters with a high surface-to-volume ratio, as depicted in Figure 3b. Upon deposition of Fe in UHV, this system initially contained the metallic Fe⁰ and other oxidized states of iron. We note that Fe^{δ+} probably corresponds to just partially oxidized Fe atoms, which have donated electrons to the ceria surface but without transforming into an oxidized phase of Fe. Similar δ+ atomic charges have been detected for other ceria-supported transition metals.^{56,57} It is worth noting that we observed a gradual decrease of Fe⁰ and Fe^{δ+} and a simultaneous increase of Fe²⁺ and Fe³⁺ components during the spectrum acquisition in Figure 8a (acquisition time was around 1 h). Subsequently, upon finishing LEED and STM experiments (after 24 h), the Fe⁰ and Fe^{δ+} components disappeared completely, as shown in Figure 8c, while the FeO_x on the surface remained in the form of small clusters. The spontaneous, albeit slow, oxidation of Fe⁰ and Fe^{δ+} species in UHV is an indication of O migration from the ceria surface to the supported FeO_x particles. After annealing this surface at 700 K in 1 × 10^{−8} mbar of O₂, the FeO_x rearranged and formed the well-ordered 2D FeO_x layer, as shown in Figure 6, with about a 5:1 Fe³⁺/Fe²⁺ ratio (Figure 8e).

The Fe 2p spectrum in Figure 8b corresponds to the surface featuring large FeO_x clusters, as illustrated in Figure 5c. Similar to the surface with small clusters, the XPS spectrum contains higher oxidation states of Fe as well as states attributed to Fe^{δ+} and Fe⁰, despite iron being deposited onto the surface in the 1 × 10^{−8} mbar of O₂. Obviously, the oxygen supplied during the deposition at 600 K was not sufficient to fully oxidize the iron deposit, resulting in the presence of Fe⁰ species. This metallic iron is presumably located within noninterfacial regions (i.e., bulk and/or surface positions of the upper layers) of the large clusters. After the following STM and LEED measurements (Figure 8d), the average Fe oxidation state on the surface remained almost unchanged, indicating that the interface FeO_x region or the FeO_x layer on the surface of large clusters impedes further oxygen diffusion into the clusters at 300 K. Complete oxidation of Fe was only achieved after an additional 20 min annealing in 1 × 10^{−8} mbar of O₂ at 600 K, as shown in the bottom-right spectra of Figure 8. At this stage, the Fe³⁺/Fe²⁺ ratio is about 2.5:1, indicating that even after prolonged oxygen exposure at elevated temperatures, Fe atoms within FeO_x clusters are, on average, less oxidized than those within the 2D FeO_x layer.

In the SRPES experiment presented in Figure 4 we gradually annealed the sample in UHV. The Fe³⁺/Fe²⁺ ratio measured from the Fe 3p spectra stabilized at about 3:1, aligning more closely with the scenario observed with large FeO_x clusters, as determined by XPS. The Fe⁰ component in this set of spectra was not observed from the beginning, indicating rapid oxidation of rather small clusters immediately after deposition. Similar to the surface depicted in Figure 5a,b, the small clusters annealed under relatively low oxygen pressure may have coalesced into larger clusters, leaving the CeO₂ surface only partially covered by the 2D FeO_x layer. The coalescence of small FeO_x particles is further evidenced by the gradual decrease in the total spectral intensity of the Fe 3p peak (Figure 4b). Furthermore, disparities

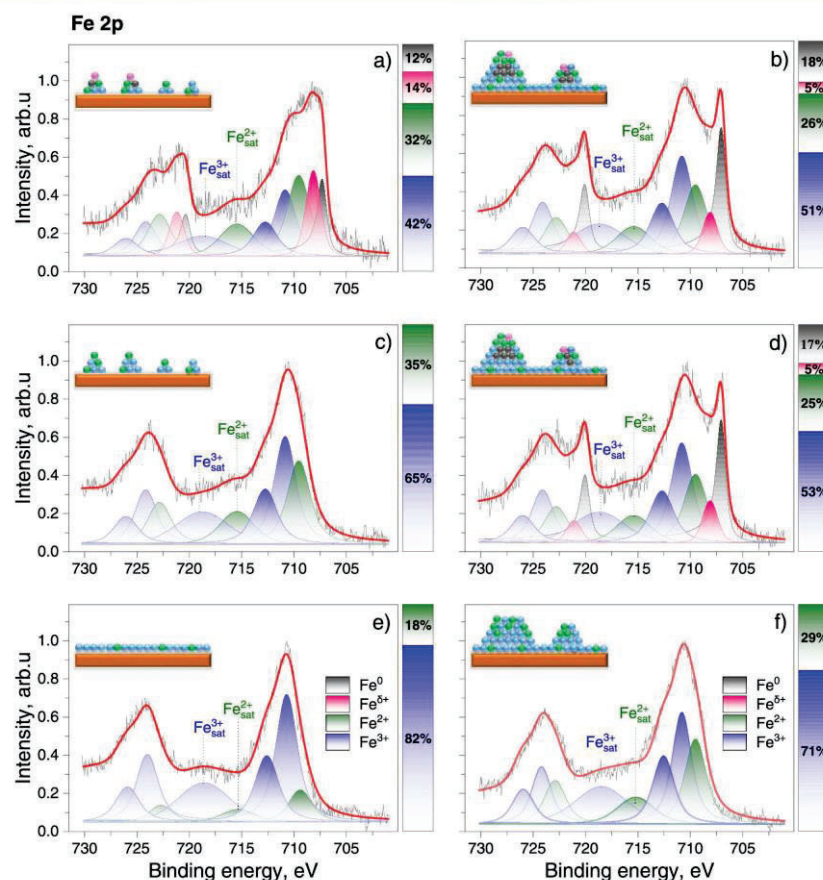


Figure 8. In situ XPS Fe 2p core level spectra showing the evolution of FeO_x/CeO₂ (111) samples with 0.7 ML Fe coverage (left) and 2 ML Fe coverage (right) after Fe deposition (a, b), STM measurement (c, d) and annealing in 1×10^{-8} mbar of O₂ (e, f). The spectra were acquired with Al K α radiation (1486.6 eV) and normalized to the same maximum height. Relative intensities of Fe³⁺, Fe²⁺, Fe³⁺_{sat} (δ ϵ (0, 2)) and Fe⁰ spectral components determined from the peak areas are specified in the columns.

in the SRPES and XPS spectra are attributable to the higher surface sensitivity of SRPES (180 eV vs 1487 eV energy of the primary radiation results in information depths of 2 vs 5 nm, respectively). Consequently, the SPRES spectra are more indicative of the Fe³⁺/Fe²⁺ ratio in the topmost surface layer of the FeO_x clusters, whereas XPS provides a representation of the ratio across entire clusters.

A dominant Fe²⁺ oxidation state of Fe atoms in the 2D layer is expected based on its structural parameters corresponding to the FeO phase, however, a dominant Fe³⁺ state (up to 5:1 ratio) is observed from our spectroscopy experiments. We address this discrepancy by means of DFT calculations. The Bader atomic charges, projected density of states (pDOS), and magnetic moments derived from the DFT calculations for the different models allow us to further characterize the electronic structure of the FeO/CeO₂(111) interface. We have focused on evaluating the charge distribution and comparing the stability between electronic states differing in the spin-alignment of the Fe cations and on the number of transferred electrons from the FeO ML to the underlying ceria substrate. As illustrated in Figure 9, this redox process leads to the oxidation of one Fe²⁺ cation to Fe³⁺ and the concomitant reduction of one Ce⁴⁺ cation

to Ce³⁺. The formal charges of the Fe and Ce cations can be inferred from their Bader charges and magnetic moments. Upon oxidizing Fe²⁺ to Fe³⁺, the (positive) Bader charge increases from 1.4 lel to 1.8 lel and the absolute magnetic moment increases from ~ 3.7 to $\sim 4.1 \mu_B$. This indicates that the donated electron is that with the opposite spin orientation than the Fe cation, consistently with Hund's rule and as illustrated in the Fe 3d pDOS in Figure 9a,c. In turn, Ce³⁺ centers exhibit a lower (positive) Bader charge than Ce⁴⁺ and a characteristic magnetic moment close to $\sim 0.9 \mu_B$ due to the occupation of a Ce 4f spin-orbital.

For the most stable structure of the smaller model, we have identified three different electronic states with zero, one, or two electrons transferred from FeO to CeO₂(111), represented in Figure 10a–c. We note that as for the free-standing FeO monolayer, the most stable electronic states for the FeO/CeO₂(111) system exhibit an antiferromagnetic ordering of the Fe cations, independently of them being Fe²⁺ or Fe³⁺. The most stable electronic state found for the FeO(2 $\times$ 2)/CeO₂($\sqrt{3} \times \sqrt{3}$) model contains only one Fe³⁺ cation (one transferred electron from FeO to CeO₂). The states with two or zero transferred electrons are 0.56 and 0.40 eV (0.14 and 0.1 eV per

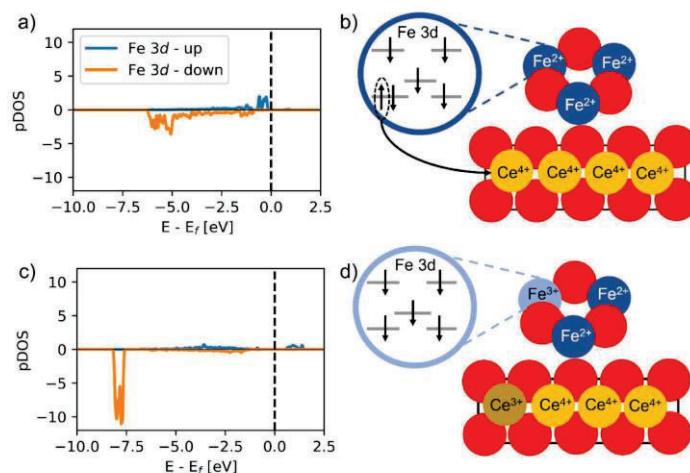


Figure 9. Electronic structure of Fe atoms in the FeO/CeO₂(111) system for different electronic states without (a and b) or with (c and d) transferred electrons from Fe 3d to Ce 4f orbitals. The density of states projected in the 3d states of Fe are shown in (a) and (c), and schemes illustrating formal Fe and Ce charges and the electronic configuration of the Fe 3d states are shown in (b) and (d).

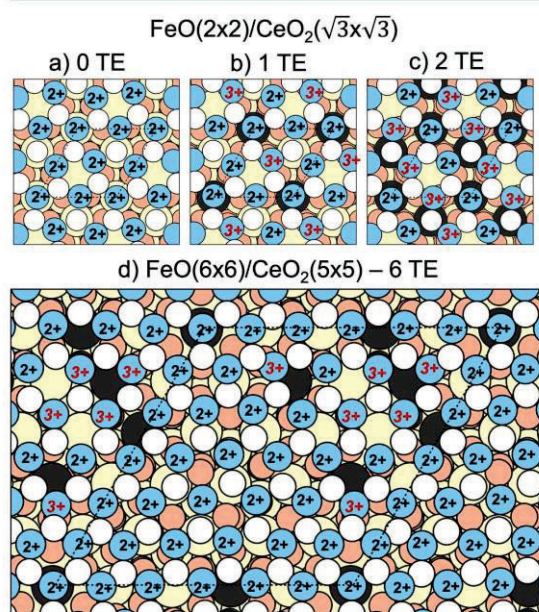


Figure 10. Different electronic states differing in the number of transferred electrons (TE) from FeO to CeO₂ in the FeO(2 × 2)/CeO₂($\sqrt{3} \times \sqrt{3}$) (a, b, and c) and FeO(5 × 5)/CeO₂(6 × 6) (d) models. Blue, white, beige, black and orange circles correspond to Fe, O_{FeO}, Ce⁴⁺, Ce³⁺ and O_{Ceria} atoms, respectively. The labels above Fe atoms indicate their oxidation state (2+ or 3+).

FeO unit) less stable, respectively. The most stable state with one transferred electron corresponds to a 1:3 Fe³⁺/Fe²⁺ ratio and 1/3 of outermost Ce atoms reduced to Ce³⁺. The concentration of Fe³⁺ is therefore lower than that measured for the FeO on CeO₂ system annealed at high temperatures.

For the larger FeO(6 × 6)/CeO₂(5 × 5) model, we have only sampled a single electronic state due to the large computational

cost of every structural relaxation. This single optimization has converged to an electronic state with 6 Fe³⁺ cations, corresponding to a 1:5 ratio between Fe³⁺ and Fe²⁺ cations, where 6 of the 25 outermost Ce cations are reduced to Ce³⁺. The distribution of the Fe²⁺, Fe³⁺, Ce³⁺, and Ce⁴⁺ cations is illustrated in Figure 10d. We have not exhaustively sampled all possible electronic states differing in the number and position of the Ce³⁺ cations formed, but for the larger model, Ce³⁺ centers generally form in the vicinity of Fe³⁺ centers.

The distribution of Fe oxidation states for both FeO/CeO₂(111) models indicates that the FeO monolayer is only partially oxidized by the ceria surface in the absence of O₂. To evaluate how exposure to O₂ would affect this distribution, we have carried out calculations with one or two additional O atoms on the FeO(2 × 2)/CeO₂($\sqrt{3} \times \sqrt{3}$) model (see Figure 11). The most stable adsorption sites for O on this system correspond to hollow sites between three Fe cations and right on top of a Ce atom of the ceria surface. O atoms adsorbed on these positions bond to the 3 Fe cations and to the Ce below, with Ce–O distances of 2.3 Å. The system with one adsorbed O atom (Figure 11a) has 2 Fe³⁺ and 2 Fe²⁺ cations, indicating that this adsorption reoxidized one Ce³⁺ to Ce⁴⁺ and one Fe²⁺ to Fe³⁺, therefore also leading to the oxidation of the Ce³⁺ center that had formed upon interaction with FeO back to Ce⁴⁺. Upon adsorption of the second O atom (Figure 11b), the two remaining Fe²⁺ cations are oxidized to Fe³⁺. The adsorption energy $E_{\text{ads}}(\text{O})$ (calculated as $E_{\text{ads}}(\text{O}) = E[\text{O-surface}] - E[\text{surface}] - 0.5E[\text{O}_2]$) of the first and second O atoms is −0.72 and −1.26 eV, respectively, which indicates that the oxidation of FeO (Fe₄O₄) to Fe₂O₃ (Fe₄O₆) is thermodynamically favorable. Here, we just added O atoms in three-Fe-coordinated sites and relaxed the structure. A more exhaustive search for stable structures of the Fe₂O₃ monolayer is likely to result in even more favorable oxidation of the ceria-supported 2D FeO.

The activity toward oxidation reactions of catalysts based on Fe and CeO₂ has been linked to the effect of Fe dopants on the oxygen storage capacity of ceria.^{5,6} Since the oxygen storage capacity of ceria-based systems depends on their reducibility,

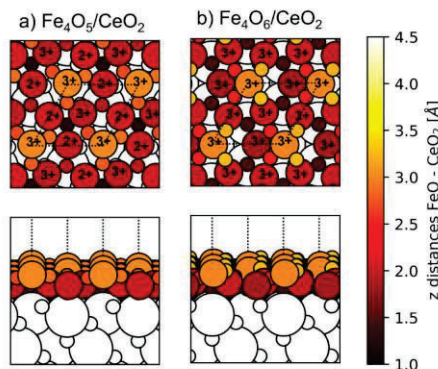


Figure 11. Oxidation of the $\text{FeO}(2 \times 2)/\text{CeO}_2(\sqrt{3} \times \sqrt{3})$ model. Structure and Fe oxidation state for the adsorption of one (a) and two (b) O atoms on $\text{FeO}(2 \times 2)/\text{CeO}_2(\sqrt{3} \times \sqrt{3})$, leading to Fe_4O_5 and Fe_4O_6 stoichiometries, respectively, of the FeO_x monolayer. White circles indicate Ce (big circle) and O (small circle) atoms of the CeO_2 support, while Fe (big colored circle) and O (small colored circle) are colored to indicate their vertical distance to the bare CeO_2 support according to the color bar on the right-hand side.

their formation energy $E_f(\text{O}_{\text{vac}})$ is often used as a descriptor for activity.^{58,59} Therefore, to establish differences between Fe-doped $\text{CeO}_2(111)$ and the $\text{FeO}_x/\text{CeO}_2(111)$ systems, we have calculated $E_f(\text{O}_{\text{vac}})$ for their corresponding models (Figures S7 and S8). $E_f(\text{O}_{\text{vac}})$ is calculated as $E_f(\text{O}_{\text{vac}}) = E(\text{X}-\text{O}_{\text{vac}}) - E(\text{X}) - 0.5E(\text{O}_2)$, where $E(\text{X}-\text{O}_{\text{vac}})$ and $E(\text{X})$ are the energies of the considered systems with and without the formed vacancy, respectively.

We start from the most oxidized states (i.e., $\text{Fe}_4\text{O}_6/\text{Ce}_9\text{O}_{18}$ for $\text{FeO}_x/\text{CeO}_2(111)$ and $\text{FeCe}_{35}\text{O}_{72}$ for Fe-doped $\text{CeO}_2(111)$). For $\text{FeO}_x/\text{CeO}_2(111)$, the first, second, and third O vacancies have $E_f(\text{O}_{\text{vac}})$ values of 1.26, 0.72, and 2.99 eV, respectively. For Fe-doped $\text{CeO}_2(111)$, the first and second O vacancies result in $E_f(\text{O}_{\text{vac}})$ of 0.43 and 1.56 eV, respectively. These results indicate that it is not significantly more favorable to form vacancies in Fe-doped $\text{CeO}_2(111)$ than on the 2D $\text{FeO}_x/\text{CeO}_2(111)$ system, and that both systems have a rich redox chemistry with readily available (i.e., low $E_f(\text{O}_{\text{vac}})$) O atoms.

4. DISCUSSION

As mentioned above, PES and STM results indicate that nonstoichiometric FeO_x clusters are formed as a result of iron–ceria interaction. The process can be described by the reaction $y\text{Fe} + x\text{CeO}_2 \rightarrow x\text{CeO}_{(2-y)} + y\text{FeO}_x$, where $x = 0 \cdots 1.5$ and $y = 0 \cdots 0.5$. Interestingly, the molar enthalpy change (ΔH_f^{m}) for the full redox reaction $\text{Fe} + 2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + \text{FeO}$ involving bulk oxides is 109.2 kJ/mol,⁶⁰ suggesting that the process is thermodynamically unfavorable at 300 K. However, it is thermodynamically more favorable to partially reduce the $\text{CeO}_2(111)$ surface than bulk ceria,⁵⁹ and to partially oxidize Fe particles than bulk Fe. A similar phenomenon has also been reported for other systems, such as Ni/CeO_2 or Co/CeO_2 , where the formation of CoO ⁶¹ and NiO ⁶² clusters was observed. The oxidation of supported metal particles by lattice O atoms of $\text{CeO}_2(111)$ is typically enabled by reverse spillover mechanism, which has been reported for even more noble metals such as Pt.⁴⁵ The spontaneous oxidation of ceria-supported 3D Fe

particles in UHV thus confirms that a reverse spillover mechanism is enabled in the $\text{FeO}_x/\text{CeO}_2(111)$ interface.

We have shown that Fe atoms, which form small clusters upon deposition, are readily oxidized to varying degrees. Conversely, bigger FeO_x clusters only oxidize after prolonged annealing in O_2 at 600 K. The slower oxidation kinetics observed in the bulk or upper layers of large FeO_x clusters, even at elevated temperatures, suggests relatively lower oxygen mobility within the superficial or interfacial iron oxide, which likely encapsulates and passivates metallic cores of the Fe clusters.

In a 2D configuration, the (111) planes of both CeO_2 ($a_{\text{CeO}_2}^{(111)} = 0.382 \text{ nm}$)⁶³ and FeO ($a_{\text{FeO}}^{(111)} = 0.31 \text{ nm}$)⁵⁰ surfaces exhibit hexagonal symmetry, indicating their potential for epitaxial arrangement. Although significant lattice mismatches, such as that between the FeO and $\text{CeO}_2(111)$ (exceeding 20%), often prevent epitaxial growth, that is not always the case. Instead of just the lattice mismatch, the growth of one oxide on another is also governed by the stability of the oxide–oxide interface and the process kinetics.⁶⁴ The modification of the surface free energy $\Delta\gamma$ induced by a film formation on a substrate can be written as $\Delta\gamma = \gamma_f + \gamma_i - \gamma_s$, where γ_f and γ_s are surface free energies of a film and a substrate, respectively, while γ_i is the interface energy. If $\Delta\gamma < 0$, the formation of a wetting layer is energetically favored, while $\Delta\gamma > 0$ would lead to islanding or clustering. Taking γ_f as that of O-terminated $\text{FeO}(111)$ (1.3 J/m²),⁶⁵ γ_s as that of O-terminated $\text{CeO}_2(111)$ (0.7 J/m²),⁶⁶ and the γ_i of -0.7 J/m^2 ($-0.47 \text{ eV/FeO unit}$) calculated by DFT in this work for the $\text{FeO}/\text{CeO}_2(111)$ interface, results in $\Delta\gamma = -0.1 \text{ J/m}^2$, indicating a preference for FeO film formation on ceria. This is in line with the slight preference to form the $\text{FeO}/\text{CeO}_2(111)$ interface rather than bulk FeO derived solely from our DFT calculations. In addition to being thermodynamically favorable, the formation of the FeO films on $\text{CeO}_2(111)$ may be dominated also by other factors such as the high degree of reduction of the ceria surface after the deposition of Fe or the different formation and oxidation kinetics of 2D films and 3D FeO_x nanostructures.

Nevertheless, our DFT calculations showed that the interaction of the 2D FeO_x layer with ceria is strengthened by the structural corrugation of the 2D FeO_x layer (which can be observed experimentally by STM), by van der Waals interactions, by the further oxidation of the 2D FeO_x layer upon incorporation of additional O atoms, or by the transfer of electrons from the 2D FeO layer to the ceria substrate. The latter is analogous to the electronic metal–support interactions widely reported for ceria-supported metals.^{57,67}

5. CONCLUSIONS

This model catalyst study offers valuable insights into the intricate behavior of iron in real Fe/CeO_2 catalysts.^{3,4,6,7} The presented findings shed light on the growth dynamics and interaction between iron and ceria during thermal treatment under UHV conditions and in the presence of O_2 . Our data demonstrate that iron readily undergoes oxidation upon deposition, giving rise to small FeO_x clusters on the ceria substrate at 300 K. Upon annealing in UHV, some clusters grow into larger particles, while others disperse and form a thin FeO_x layer. Annealing in an oxygen-rich environment promotes the dispersion of iron on the ceria surface and enhances the ordering of the resulting 2D FeO_x thin film, as validated by STM and LEED. By means of DFT calculations, we showed that this 2D surface layer is thermodynamically more stable than bulk FeO or

Fe-doped CeO₂(111) due to (i) the formation of bonds between the Fe atoms and the O atoms of the ceria lattice, (ii) van der Waals interactions between the FeO_x layer and the CeO₂(111) surface, (iii) the structural corrugation of the FeO monolayer, (iv) the transfer of electrons from Fe to ceria, and (v) the additional oxidation by adsorbed oxygen.

In addition, we have proposed a method for producing stable, well-ordered epitaxial FeO_x films on a ceria support. Similar ultrathin FeO films grown on much more expensive noble metal substrates have demonstrated exceptional catalytic activity in CO oxidation reactions.⁶⁸ Thanks to the structural corrugation of the 2D FeO_x layer, this system could also serve as an excellent template for supporting ordered arrays of noble-metal nanoparticles.^{69,70} Lastly, the capacity of the 2D FeO film to donate electrons suggests that the 2D FeO/CeO₂(111) system can be used as a reducing support for catalytically active metal particles, enabling the synthesis of catalytic materials with negatively charged metal centers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.4c05542>.

Additional Fe 2p spectra fitting parameters, Fe 2p core-level spectra, valence band spectra, STM images, in situ Ce 3d core-level spectra, and DFT supporting calculations (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

Electronic and Structural Properties of Thin Iron Oxide Films on CeO₂

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The Fe 2p band exhibits a complex shape characterized by peak asymmetries, d–d multiplet splitting, and shake-up satellites typical of transition metals and their oxides. In particular, the multiplet splitting in Fe 2p spectra is due to unpaired electrons resulting in several final states in the band. The Fe²⁺ cations in the 3d⁶ initial state have no unpaired electrons, resulting in a low spin state ($S = 0$). Therefore, no multiplet splitting is expected for low spin Fe²⁺ cations. In contrast, the Fe³⁺ cations have unpaired electrons in the 3d⁵ initial state, resulting in a high spin state ($S = 5/2$)¹. Consequently, the Fe³⁺ state undergoes multiplet splitting due to the coupling of the final states with the unpaired 3d electrons, resulting in a broadened spectrum. Studies on iron oxides such as Fe₂O₃, Fe₃O₄, and FeOOH have demonstrated that the broadening of Fe 2p spectra comprises not only one asymmetric peak but the summation of several symmetric peaks.^{2–6} In our study, we adapted a fitting procedure proposed by Pauly et al. utilizing the smallest number of peaks necessary to represent the experimental data accurately.⁴ Specifically, two Voigt doublets were employed to fit the Fe³⁺ state, often referred to Fe³⁺ species with tetrahedral and octahedral occupancies.^{7–11} One Voigt doublet was utilized for the fitting of Fe²⁺ and Fe^{δ+} oxidation states, while the Doniach–Šunjić doublet was employed to represent the Fe⁰ state. We believe that Fe^{δ+} corresponds to partially oxidized FeO_x nanoparticles. Satellite features were fitted with the single Voigt peak. The fitting parameters are summarized in Table S1.

Table S1. The results of XPS Fe 2p spectra fitting for metallic Fe, Fe₂O, FeO and Fe₂O₃

	Fe ⁰	Fe ^{δ+}	Fe ²⁺	Fe ³⁺ _(Oct)	Fe ³⁺ _(Tet)
Binding energy Fe 2p _{3/2}	707.2 ^{12,13}	708.1 ¹⁴	709.5 ^{7,15}	710.8 ^{7,13,16}	712.7 ^{7,16}
Spin-orbit splitting (eV)	13 ¹⁷	13	13.3	13.3 ⁸	13.3 ⁸
Branching ratio	0.5	0.5	0.52	0.52 ⁸	0.52 ⁸
Lorentzian width (eV)	0.6	0.6	1.6	1.6	1.7
Gaussian width (eV)	0.6	1.4	1.6	1.4	1.6
Binding energy satellite (eV)	-		715.4 ¹⁵	718.7 ¹⁵	

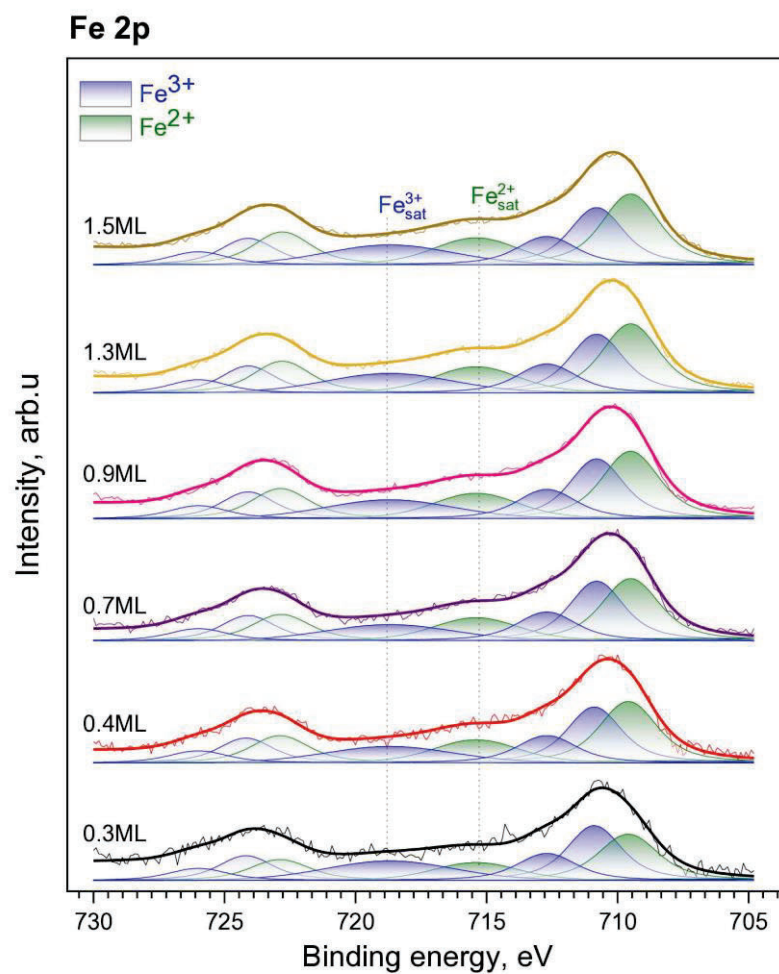


Figure S1. Fe 2p core level spectra obtained by XPS for stepwise deposition of iron on ceria. The spectra were acquired with Mg K α radiation (1253.6 eV) and normalized to maximum height.

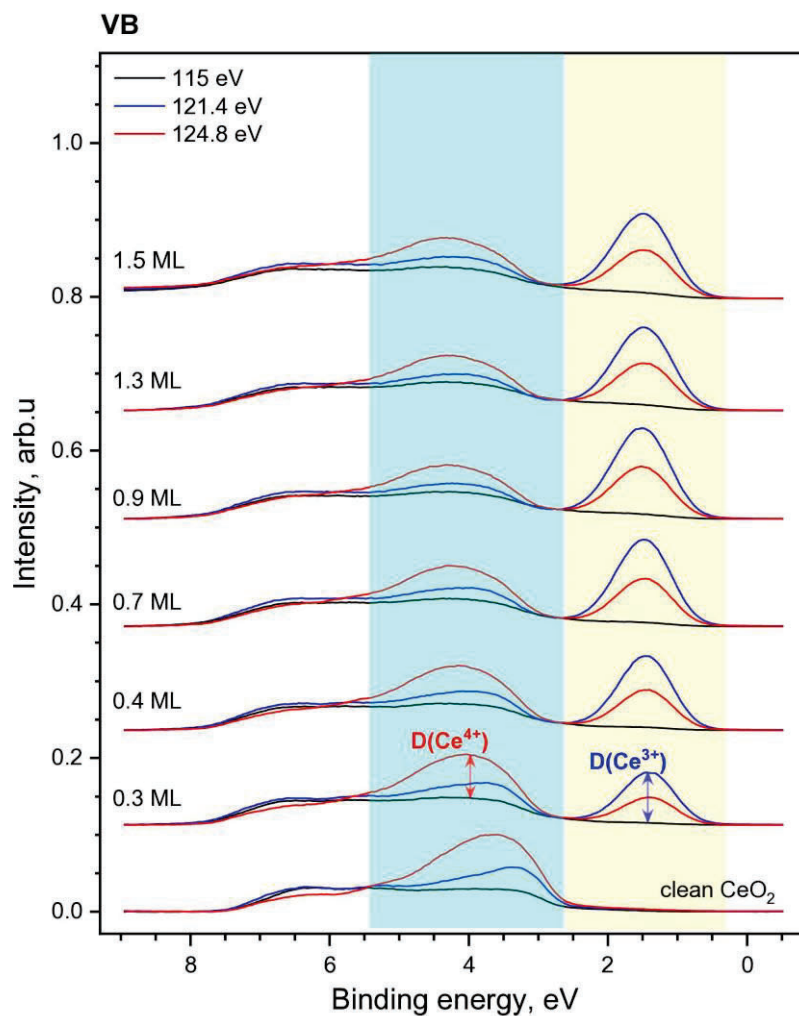


Figure S2. Valence band (VB) spectra obtained during stepwise deposition of Fe onto the CeO₂(111) surface at 300 K in UHV at 115 eV (off-resonance), 121.4 eV (Ce³⁺ resonance) and 124.8 eV (Ce⁴⁺ resonance) photon energy. The arrows show resonance enhancements $D(\text{Ce}^{3+})$ and $D(\text{Ce}^{4+})$.

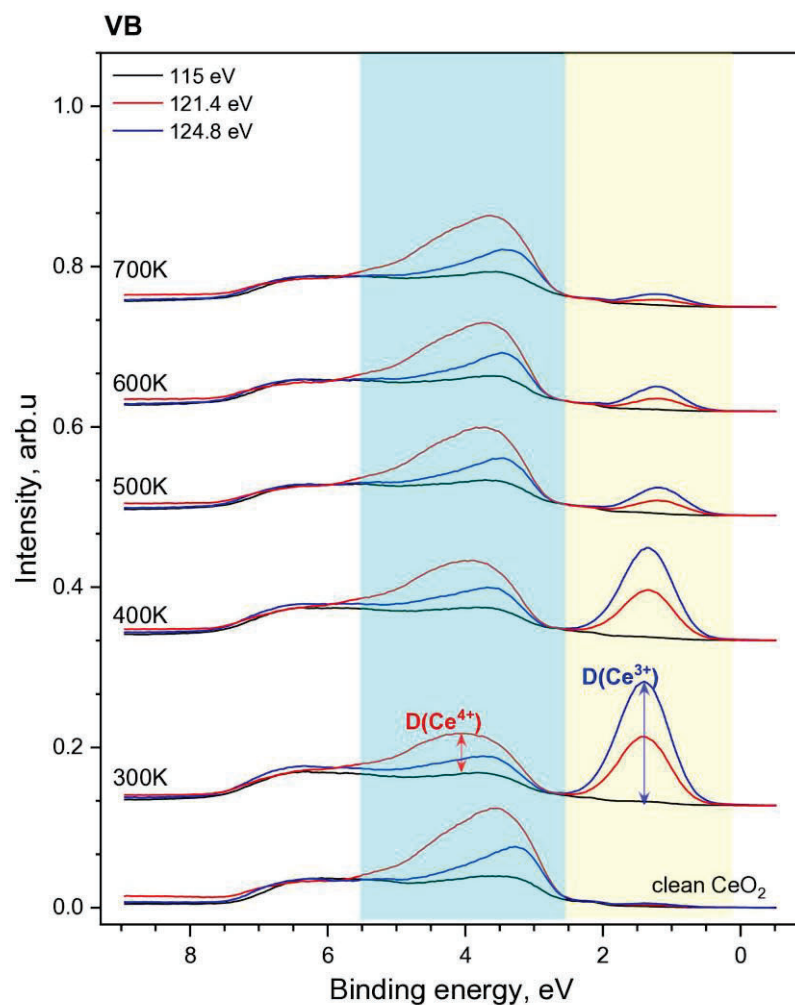


Figure S3. Valence band (VB) spectra acquired from the 0.7 ML of Fe on the $\text{CeO}_2(111)/\text{Cu}(111)$ system in UHV at different temperatures at 115 eV (off-resonance), 121.4 eV (Ce^{3+} resonance) and 124.8 eV (Ce^{4+} resonance) photon energy. The arrows show resonance enhancements $\text{D}(\text{Ce}^{3+})$ and $\text{D}(\text{Ce}^{4+})$.

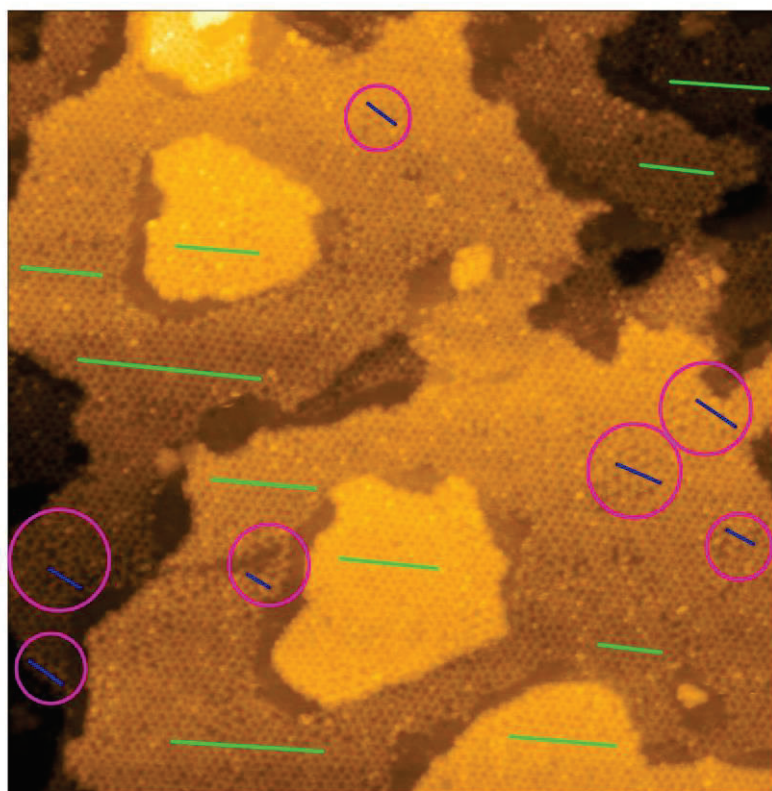


Figure S4. STM image of the $\text{FeO}_x/\text{CeO}_2(111)$ surface prepared by deposition of about 0.7 ML of Fe on the $\text{CeO}_2(111)$ substrate at 300 K and annealing at 800 K in 1×10^{-8} mbar of O_2 . Surface area $110 \times 110 \text{ nm}^2$, $U_{\text{bias}} \approx 3 \text{ V}$, $I_t \approx 10 \text{ pA}$. Most of the surface is covered by the FeO_x superstructure (marked by green lines) rotated by 30° with respect to the substrate lattice. Minority superstructures better aligned with the substrate are marked by magenta circles.

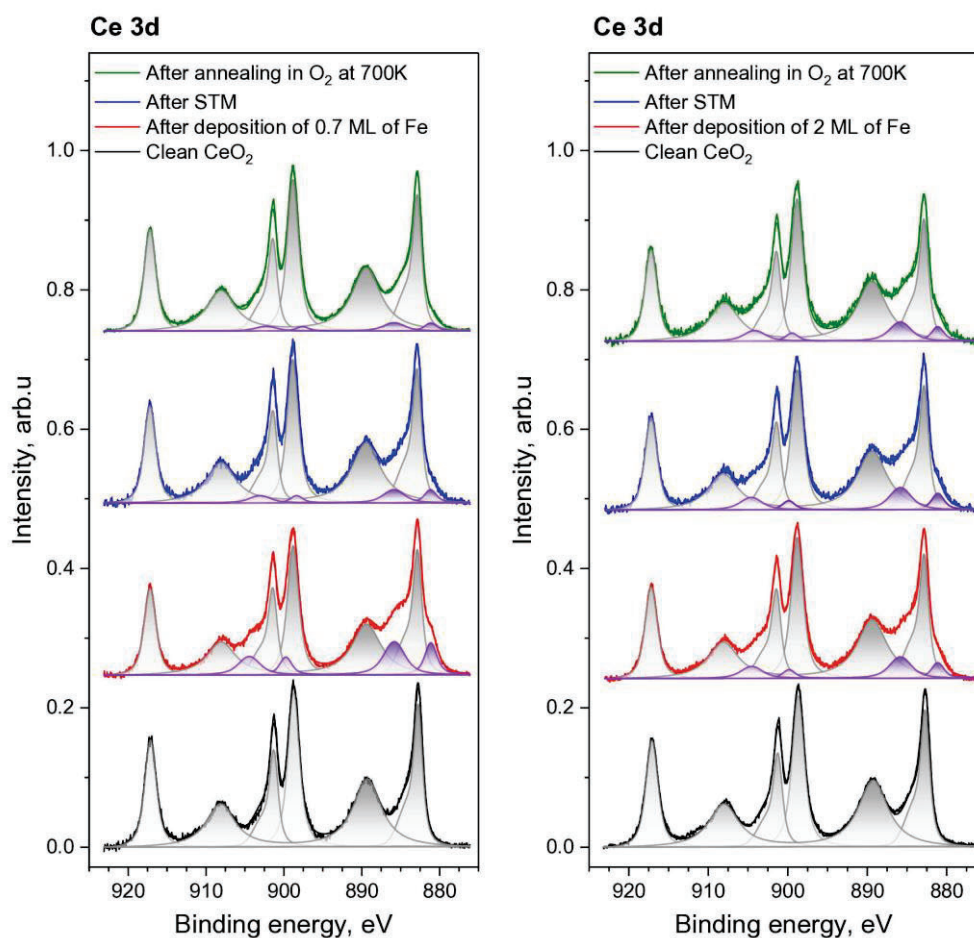


Figure S5. The in-situ XPS Ce 3d core level spectra from the clean CeO₂(111) surface as well as after the deposition of 0.7 ML (left) and 2 ML of iron (right), after the STM experiment and after annealing in 1×10^{-8} mbar of O₂. The spectra were acquired with Al K α radiation (1486.6 eV) and were normalized to the same area. Three Ce⁴⁺-related doublets are marked in gray and two Ce³⁺-related doublets are marked in violet. Deconvolution of the Ce 3d spectra was performed following the procedure described in ref. [18].

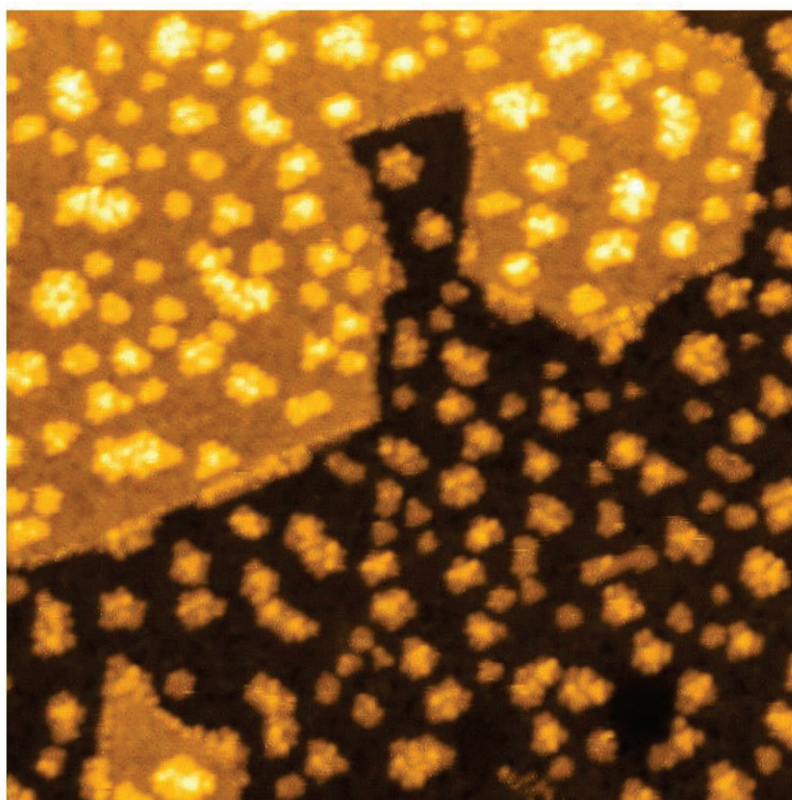


Figure S6. STM image of the FeO_x/CeO₂(111) surface prepared by deposition of about 0.2 ML of Fe on the CeO₂(111) substrate at 300 K and annealing at 700 K in UHV. Surface area $70 \times 70 \text{ nm}^2$, $U_{\text{bias}} \approx 3 \text{ V}$, $I_t \approx 10 \text{ pA}$.

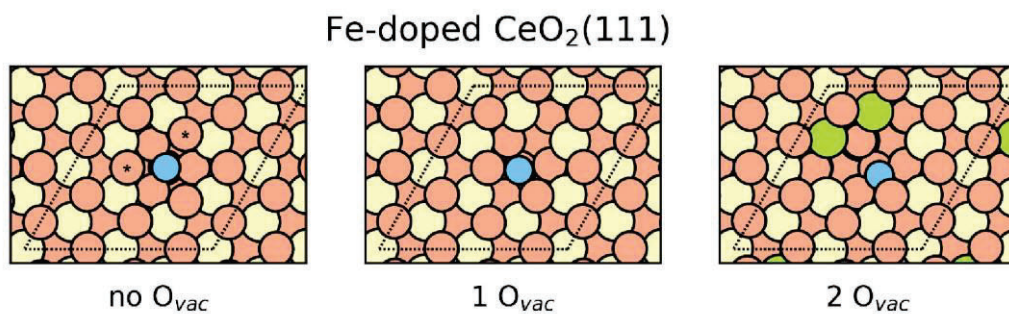


Figure S7: Relaxed structures of the models used to represent the fully oxidized and reduced Fe-doped $\text{CeO}_2(111)$ surface. An outermost Ce atom has been replaced by a Fe atom in the $\text{CeO}_2(2\sqrt{3} \times 2\sqrt{3})$ slab model, leading to 1/12 coverage of Fe. To form oxygen vacancies, O atoms bonded to the Fe atom (indicated with asterisks in the left image) have been removed from the outermost O layer. Blue, beige, green, and orange circles correspond to Fe, Ce^{4+} , Ce^{3+} , and O ceria atoms, respectively.

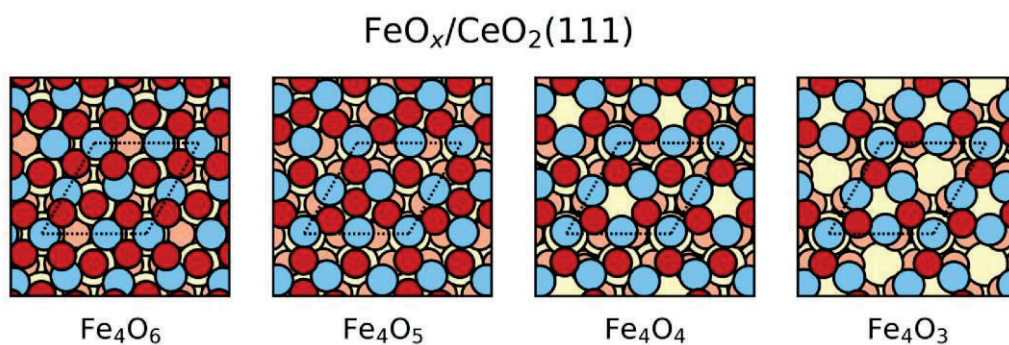


Figure S8: Relaxed structures of the models used to calculate $E_f(\text{O}_{\text{vac}})$ in $\text{CeO}_2(111)$ -supported 2D FeO_x . Blue, red, beige and orange circles correspond to Fe, O atoms in FeO and Ce, O atoms in CeO_2 , respectively.

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Chapter 5: Low temperature CO oxidation reaction catalyzed by supported PtO_x clusters

5.1 Introduction

CO oxidation is a relevant process for the conversion of exhaust gases^{1,2} and an important test reaction for heterogeneous catalysis.³ Substantial efforts for the development of efficient catalysts for this reaction have been made, with proposed catalysts ranging from noble metals to oxide-based materials.^{4–8}

Cerium dioxide (CeO₂) is one of the widely used oxide materials for oxidation reactions in heterogeneous catalysis,^{9–11} given its prominent oxygen storage capacity and the abilities of modifying chemical properties of metal particles supported thereon, through metal-support interactions (MSI).^{12–14}

MSI have proven to facilitate improving the efficiency of CeO₂-based oxidation catalysts, in particular, to lower the temperature required for starting the CO oxidation.¹⁵ Platinum supported on CeO₂ surface reveals strong oxidative catalytic activity partly related with its high structural diversity resulting in a variety of exposed surface active species ranging from single atoms (ions) and small clusters to nanoparticles.^{16–25} The structural diversity of the Pt/CeO₂ catalytic materials makes several CO oxidation mechanism possible, of which the Langmuir-Hinshelwood (LH) and Mars-van Krevelen (MvK) mechanisms are typically discussed to explain the catalytic activity towards CO oxidation.^{20,26,27}

Another characteristic of Pt supported on CeO₂ is that already under quite mild oxidizing conditions, Pt particles can react with gas-phase O₂ molecules to form oxidized PtO_x species,^{28–33} which revealed significant catalytic activity in the CO oxidation starting at temperatures as low as -40°C.^{32,34} This low temperature activity of PtO_x species cannot be explained by the LH or MvK mechanism, since their rate determining step (RDS) involves too high activation energy to break O-O bonds (LH) or to create surface O vacancies (MvK). For the MvK, an activation energy of 0.9 eV has been reported²⁴ with computational kinetic studies showing CO oxidation catalytic activity well above room temperature.²⁷ So far, there are no mechanistic insights in the literature that unambiguously rationalize the observed CO oxidation catalytic activity of PtO_x particles supported on CeO₂ below 0°C.

The objective of this chapter is to use density functional theory to evaluate the reactivity of a Pt₆O₉/CeO₂(111) model system towards CO and O₂, to propose reaction mechanisms that can

rationalize the high CO oxidation catalytic activity of Pt/CeO₂ nanomaterials observed below room temperature and to perform kinetic Monte Carlo simulations to address the relevancy of the proposed mechanisms for the low temperature CO oxidation.

5.2 Computational Models

A Pt₆O₉ cluster supported on CeO₂(111) is used as the structural model for this chapter (Figure 5.1). This model was taken from an ab-initio thermodynamic study performed by Quinlivan Dominguez et al. (ref. 35) where this cluster was shown to be the most stable under oxidizing conditions of various ceria-supported species comprising 6 Pt atoms.

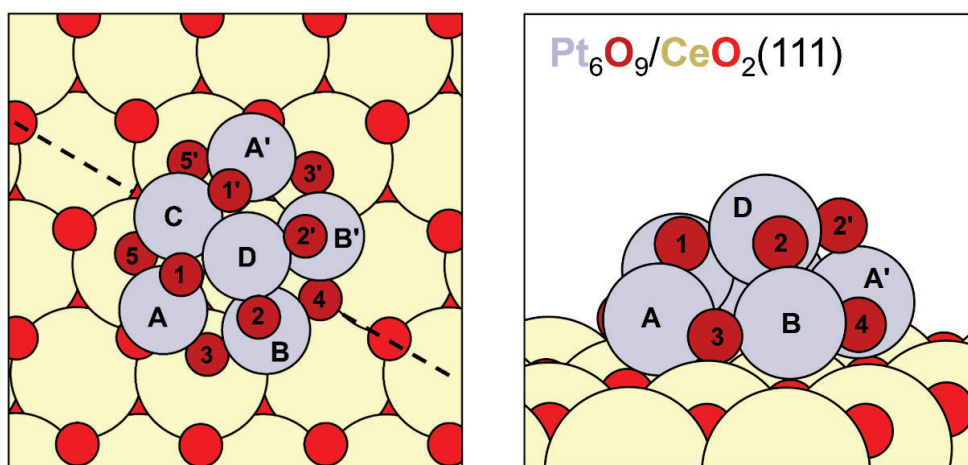


Figure 5.1: Structural model of Pt₆O₉ cluster supported on CeO₂(111) surface. Grey, dark red, beige and light red balls are Pt, O of Pt₆O₉, Ce and O of CeO₂ atoms, respectively. Atoms in the Pt₆O₉ cluster are labeled with capital letters (Pt) and numbers (O). The dashed line corresponds to a symmetry plane of the cluster, which makes atoms with primed and non-primed labels equivalent. The left-hand side panel is a top view of the model and the right-hand side is a side view.

The CeO₂ surface is represented by two O-Ce-O tri-layers and a 4×4 surface supercell with 12 Å of vacuum in the z direction, where the bottom tri-layer is fixed on bulk positions with an optimized lattice parameter of 5.49 Å.

5.3 Kinetic Simulations

Kinetic Monte Carlo Simulations were performed within the first reaction method³⁶ implemented in the MonteCoffee package.³⁷ The active sites on the Pt₆O₉ cluster are considered independent from each other and a list of neighbors is constructed to define the connectivity of Pt atoms to surrounding O atoms and the reactive events possible for a given site. Simulations were performed in the temperature range from -100°C to 100°C and 10 simulations were done for each temperature to ensure the statistical accuracy.

5.4 Results

The reactivity of the Pt₆O₉ cluster supported on the surface of CeO₂ can be evaluated by the adsorption energies of CO molecules. The calculated CO adsorption energies on top of different Pt atoms of the supported Pt₆O₉ cluster are shown in Table 5.1.

Pt atom	E _{ads} (CO), eV
C	-0.86
D	-0.83
A (A')	-0.69
B (B')	-0.19

Table 5.1: Adsorption energy of CO on different Pt atoms of the Pt₆O₉ cluster supported on CeO₂(111). Pt atoms are labeled as specified in Figure 5.1.

The adsorption energy of CO is calculated as follows:

$$E_{\text{ads}} = E(\text{CO}_{\text{top}}\text{-Pt}_6\text{O}_9/\text{CeO}_2) - E(\text{Pt}_6\text{O}_9/\text{CeO}_2) - E(\text{CO}),$$

where $E(\text{CO}_{\text{top}}\text{-Pt}_6\text{O}_9/\text{CeO}_2)$ and $E(\text{Pt}_6\text{O}_9/\text{CeO}_2)$ are, respectively, the total energies of the Pt₆O₉/CeO₂ system with and without CO adsorbed on top of a Pt atom, while $E(\text{CO})$ is the total energy of the gas-phase CO molecule.

Another aspect of the reactivity of the Pt₆O₉ cluster is how strongly bound its O atoms are. This can be assessed by calculating the O vacancy formation energy $E(\text{O}^v)$:

$$E(\text{O}^v) = E(\text{Pt}_6\text{O}_8\text{v}(\#)/\text{CeO}_2) + 1/2 * E(\text{O}_2) - E(\text{Pt}_6\text{O}_9/\text{CeO}_2),$$

where $E(\text{Pt}_6\text{O}_8\text{v}(\#)/\text{CeO}_2)$ is the total energy of a reduced Pt₆O₈ cluster with an O vacancy in the O site # labeled according to Figure 5.1. $1/2E(\text{O}_2)$ is the energy of one O atom in the free O₂ molecule defined as a half of its total energy $E(\text{O}_2)$. The O vacancy formation energies for the Pt₆O₉ cluster supported on CeO₂(111) are listed in Table 5.2.

O atom	E(O ^v), eV
2 (2')	1.71
1 (1')	1.76
5 (5')	1.92
4	2.17

Table 5.2: O vacancy formation energy $E(O^v)$ for the Pt_6O_9 cluster supported on the $CeO_2(111)$ surface calculated with respect to a half of the total energy of free O_2 molecule. The labels for the oxygen atoms correspond to those in Figure 5.1.

From Figure 5.1, O^1 and O^2 atoms are not in direct contact with the $CeO_2(111)$ support. Therefore, these atoms are called herein as top layer ones, while the atoms O^3 , O^4 and O^5 are called bottom layer atoms. It is important to note that the O vacancy formation energies from the cluster are substantially lower than the O vacancy formation energy from the $CeO_2(111)$ slab with the O atom closest to the Pt_6O_9 cluster (Pt^A) characterized by $E(O^v) = 3.02$ eV.

Considering the reactivity of the supported Pt_6O_9 cluster with respect to CO (Table 5.1) and oxygen (Table 5.2), the oxidation of a CO molecule proceeds through the formation of activated O-CO complexes, with formation energies

$$\Delta E_f(O-CO) = E(O-CO-Pt_6O_9/CeO_2) - E(CO_{top}-Pt_6O_9/CeO_2),$$

where $E(O-CO-Pt_6O_9/CeO_2)$ is the total energy of the O-CO complex adsorbed on the Pt_6O_9 cluster. Then, the subsequent CO_2 desorption energy is calculated as:

$$\Delta E_{des}(CO_2) = E(Pt_6O_8(v\#)/CeO_2) + E(CO_2) - E(O-CO-Pt_6O_9/CeO_2),$$

where $E(CO_2)$ is the total energy of a gas-phase CO_2 molecule.

Energies for the process of CO oxidation are listed in Table 5.3, showing the formation of O-CO complexes on different adsorption sites of Pt_6O_9/CeO_2 , the activation energy of such process and the desorption energy of CO_2 .

O-CO/Pt	$\Delta E_f(O-CO)$, eV	$E^\ddagger$, eV	$\Delta E_{des}(CO_2)$, eV
1A	-1.23	0.32	-0.30
1C	-1.15	0.45	-0.38
1D	-1.38	0.30	-0.14
2D	-1.82	0.52	0.24
3A	-1.24	0.10	0.19
5A	-1.03	0.43	-0.33

5C	-1.49	0.39	0.13
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Table 5.3: Energies of the activated O-CO complexes adsorbed on Pt₆O₉/CeO₂. The adsorption site is indicated by labels of the O atom reacting with CO and the Pt atom where CO is adsorbed, as defined in Figure 5.1. $\Delta E_f(\text{O-CO})$ is the formation energy of O-CO/Pt, $E^\ddagger$ is the activation energy for this reaction and $\Delta E_{\text{des}}(\text{CO}_2)$ is the desorption energy of CO₂ from the O-CO/Pt complex.

The desorption of CO₂ results in a reduced Pt₆O₈ cluster, where the O vacancy can be located in the top layer (atom O¹ – site v1) or in the bottom layer (atom O³ – site v3), since the formation of these sites requires the smallest activation energy. The Pt₆O₈ can be re-oxidized by the adsorption of a gas-phase O₂ molecule in the available vacancy site, resulting in a Pt₆O₁₀ cluster with an extra O atom available for the second CO oxidation reaction. This reaction path follows the reactant sequence +CO/+O₂/+CO to form a closed catalytic cycle.

The adsorption energy of O₂ on the vacancy sites v1 and v3 are -1.67 eV and -1.84 eV, respectively. On the resulting Pt₆O₁₀, the adsorption and activation of CO leading to CO₂ desorption follows a similar path to the first CO₂ desorption reaction, i.e. the formation of an activated O-CO/Pt complex as an intermediate step to CO₂ desorption. The energy values for these reactions are shown in Table 5.4.

Site	$E_{\text{ads}}(\text{CO})$, eV	$E^\ddagger$, eV	$\Delta E_{\text{des}}(\text{CO}_2)$, eV
Pt ^A v1	-0.49	0.76 ^a	-2.88
Pt ^C v1	-0.43	0.99 ^a	
Pt ^D v1	-0.51	0.17	-2.86
Pt ^A v3	-0.52	0.56 ^b	-3.16

a) Transition states structures of these high activation barriers were calculated with lower accuracy.

b) Transition state corresponds to desorption of CO₂ instead of O-CO formation.

Table 5.4: Adsorption energies of CO ($E_{\text{ads}}(\text{CO})$) on Pt sites of Pt₆O₁₀ near an O₂ molecule adsorbed in a vacancy site v1 or v3. $E^\ddagger$ is the activation energy for O-CO formation and $\Delta E_{\text{des}}(\text{CO}_2)$ is the desorption energy of CO₂.

With the desorption of the second CO₂ molecule, a full catalytic cycle is described. Since the O atoms from the cluster involved are different, we can label the resulting cycles as the top layer cycle (Figure 5.2) and the bottom layer cycle (Figure 5.3).

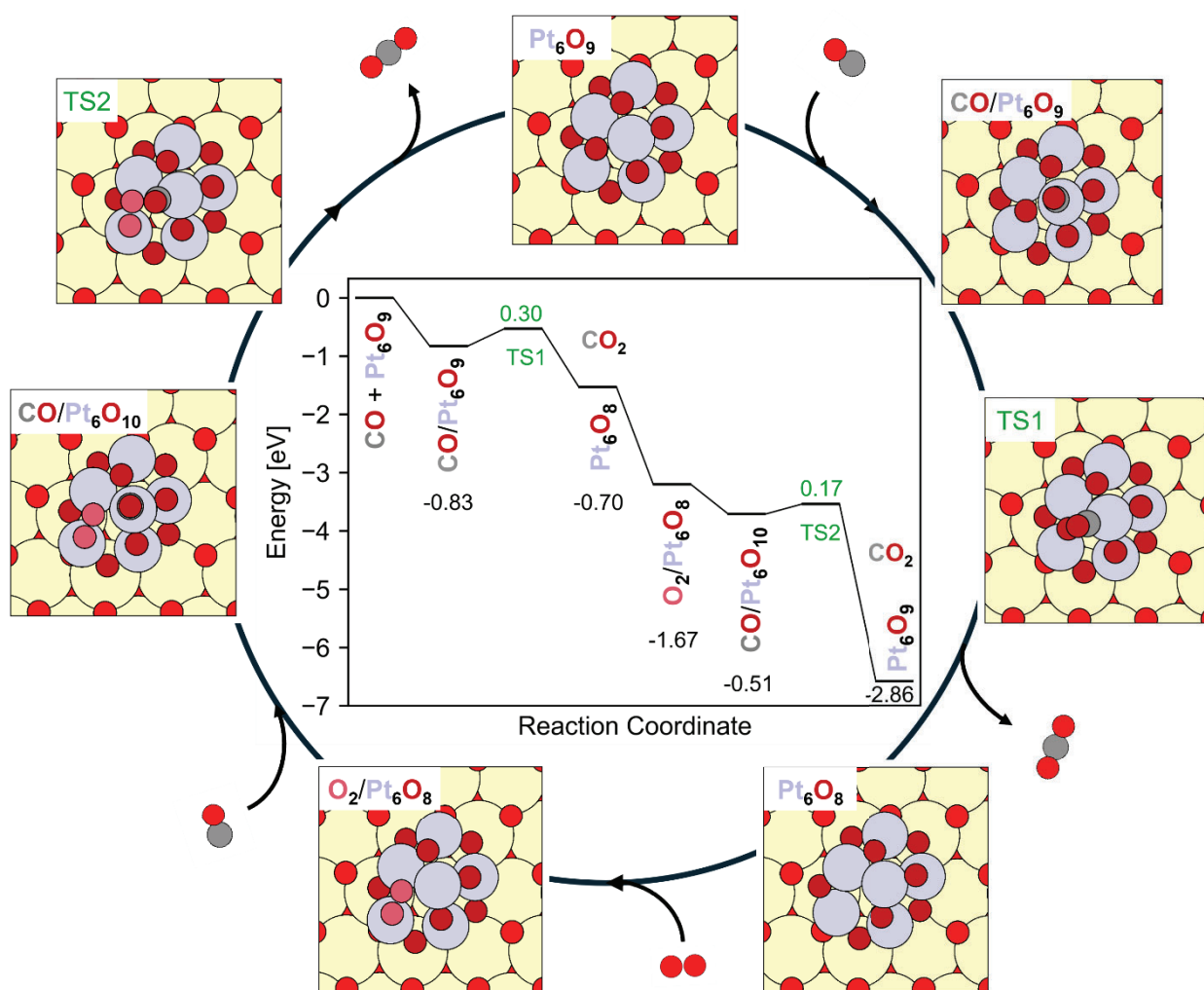


Figure 5.2: Potential energy diagram of the top layer catalytic cycle for CO oxidation. The O atom from the cluster involved in this cycle belongs to the top layer of the Pt₆O₉ cluster. The energy values in the diagram are the changes in energy with respect to the previous step in the reaction coordinate. Values in green correspond to the calculated activation energies.

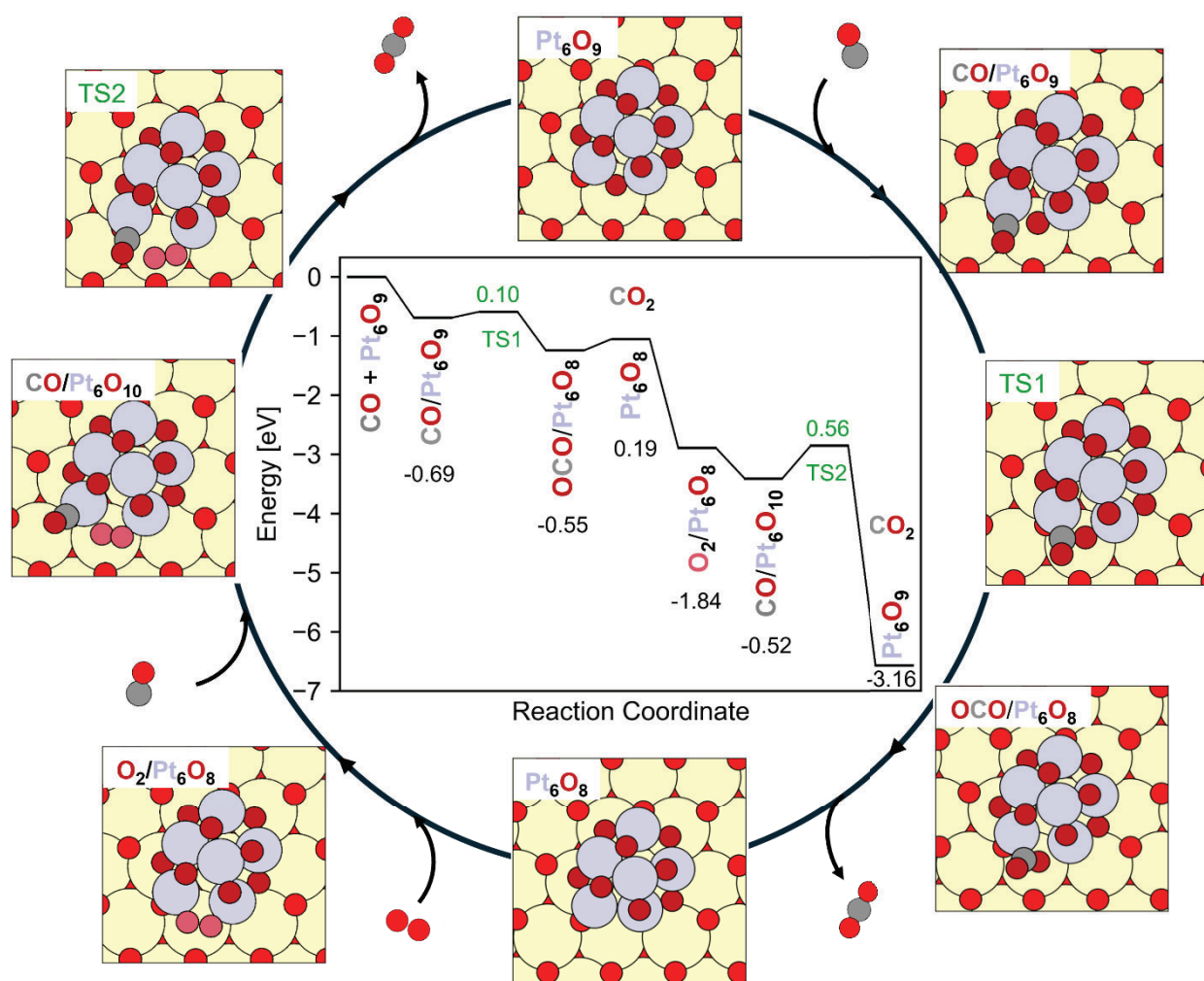
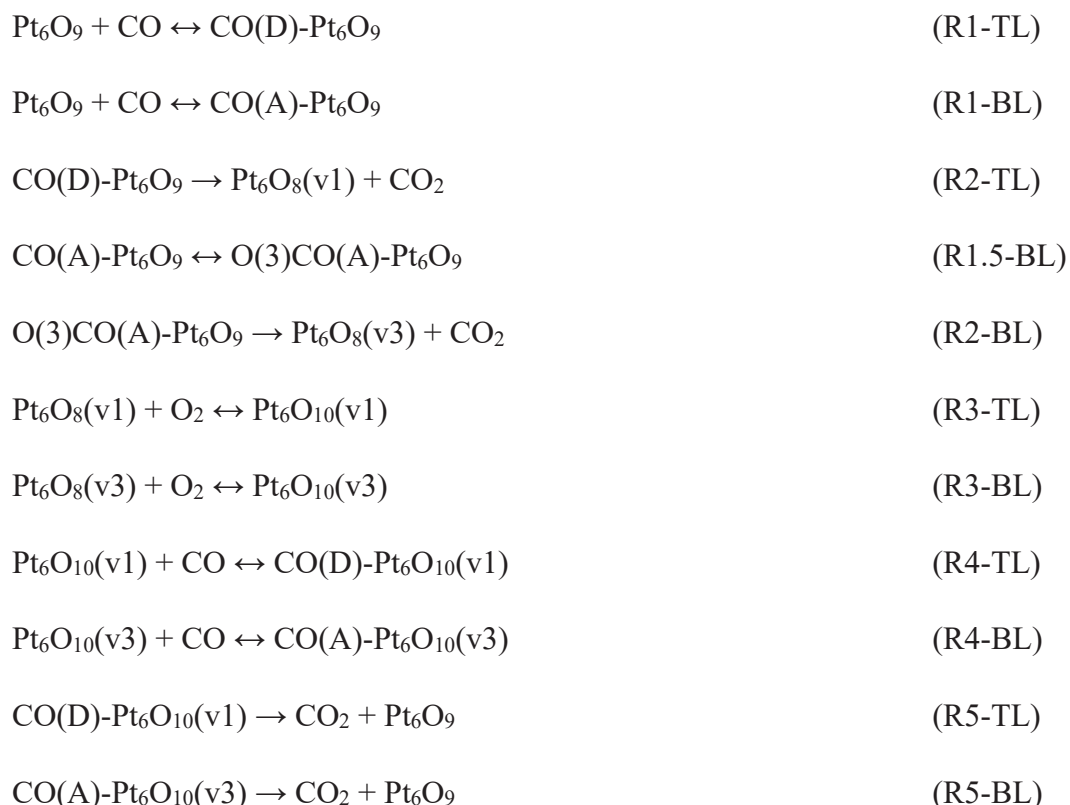


Figure 5.3: Potential energy diagram of the bottom layer catalytic cycle for CO oxidation, involving O atoms from the bottom layer of the Pt₆O₉ cluster. The energy values in the diagram are the change in energy with respect to the previous step in the reaction coordinate. Values in green are the activation energies.

The rate determining step (RDS) for the top layer cycle (Figure 5.2) is characterized by the activation energy 0.30 eV, while the desorption of the second CO₂ molecule requires the activation energy 0.17 eV. The bottom layer cycle has an activation energy 0.19 eV for the desorption of the first CO₂ molecule and 0.56 eV for the second CO₂ molecule, making the second CO₂ desorption the RDS of this catalytic cycle.

To evaluate the activity of the proposed mechanism described for the top layer and bottom layer catalytic cycles in Figures 5.2 and 5.3, adsorption and activation energies are used as input for kinetic Monte Carlo (kMC) simulations. The reaction list is:



Here, reactions R1 to R5 represent each step of the catalytic cycles previously described, with a reactant sequence of CO/O₂/CO. The labels TL and BL describe the top layer and the bottom layer cycles, respectively. R1 and R4 are CO adsorption/desorption steps and R2 and R5 are CO₂ desorption steps, with the intermediate step R1.5-BL in the case of the bottom layer cycle. R3 is the adsorption/desorption step of O₂ on the vacancy site created by the CO₂ desorption in step R2.

Calculated turnover frequencies (TOF) are shown in Figure 5.4. The TOF value for the top layer cycle at -40°C is similar to the TOF value reported for CO oxidation on metallic (not oxidized) Pt particles supported on CeO₂ at much higher temperature around 100°C.

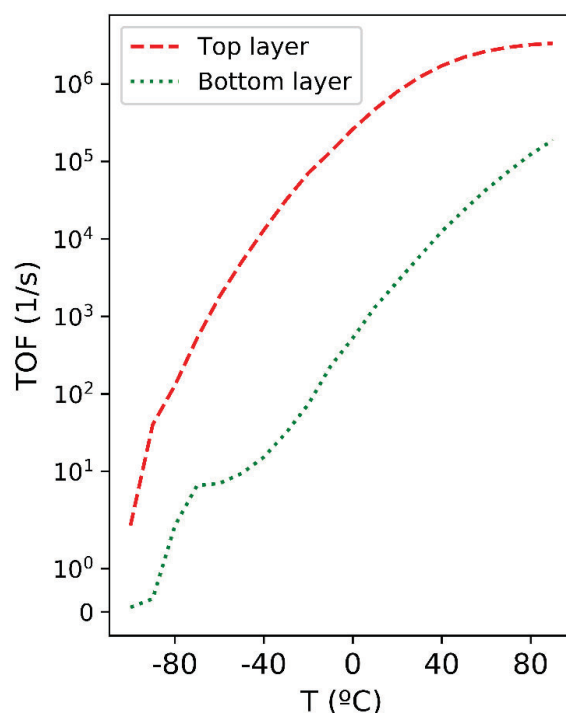


Figure 5.4: Calculated turnover frequency (TOF) values in temperature range from -100 to 100 °C for the CO oxidation taking place according to the catalytic cycles shown in Figures 5.2 and 5.3: red line – top layer cycle, green line – bottom layer cycle.

The TOF values of the bottom layer cycle are notably smaller, by 2-3 orders of magnitude, than the top layer cycle values in temperatures from -60°C to 60°C. The difference of the RDS between bottom layer and top layer cycles drive the kinetics of the process below room temperature.

5.5 Conclusions

The CO oxidation reactivity of the Pt_6O_9 cluster supported on $\text{CeO}_2(111)$ was studied by means of DFT calculations and kMC simulations. The reactivity was determined by analyzing CO adsorption and O vacancy formation. The latter reveals easily removable O atoms with vacancy formation energies by 0.8 to 1.3 eV smaller than O vacancy formation energies in the $\text{CeO}_2(111)$ support at the interface with the Pt_6O_9 cluster.

These easily removable O atoms enable an alternative reaction pathway that rationalizes atomic-level reasons for CO oxidation reaction taking place below room temperature. O atoms from the cluster as well as gas-phase O_2 are involved in CO oxidation with the activation energies from 0.10 to 0.56 eV.

A reaction mechanism is proposed, where two different catalytic cycles comprising O atoms from the top layer and from the bottom layer of the cluster are evaluated. The most favorable reaction mechanism involves a reactant sequence of +CO/+O₂/+CO, with the top layer cycle and the bottom layer cycle having a RDS with the activation barriers 0.30 eV and 0.56 eV, respectively.

Using DFT reaction and activation energies as inputs for kMC simulations results in the catalytic activity for CO oxidation at temperatures around -40°C, with the TOF as high as that reported at 100°C for metallic (not oxidized) Pt supported on CeO₂(111). This strongly suggests that the CO oxidation activity at temperatures well below room temperature is mediated by Pt oxide clusters and gas-phase O₂, with CeO₂(111) support acting essentially as a spectator in the proposed reaction mechanisms.

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5.7 Publication

How Pt/CeO₂ Nanostructures Can Catalyze CO Oxidation at Very Low Temperature

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Abstract.

Calculated activation barriers for CO oxidation on Pt/CeO₂ catalysts in the literature exceed 0.9 eV. This is inconsistent with the experimentally observed CO oxidation at temperatures below 0°C, characterized by the activation barriers of ca. 0.1 eV. This study addresses this problem by DFT modelling of various CO oxidation pathways on supported platinum-oxide (PtO_x) clusters, which were shown by us to be stable even at very low oxygen pressure. These reaction pathways involve oxygen of PtO_x clusters and gas phase O₂ and not lattice oxygen of

the CeO₂ support. Our calculations showed that CO adsorbed on PtO_x clusters can be pre-oxidized with an activation barrier as low as 0.3 eV by forming bent O-CO intermediates with reactive O atoms of the clusters and then desorb as CO₂. Gas-phase O₂ heals thus created O vacancies and provides O atoms for the subsequent CO oxidation to complete the catalytic cycle. According to the kinetic simulations using our DFT data the proposed CO oxidation mechanisms are consistent with the experimental observations of the high catalytic activity well below room temperature. These new mechanistic insights pave the way for designing oxidation catalysts at very low temperatures, which are not based on precious metals.

Introduction

CO oxidation is an important process for conversion of toxic exhaust gases.^{1,2} It is also a test reaction for obtaining fundamental insights in the heterogeneous catalysis.^{3,4} Significant efforts have been devoted to developing efficient CO oxidation catalysts ranging from noble metals^{5,6} to oxide-based materials.^{7,8} Among the latter, cerium dioxide (CeO_2 , ceria)⁹ has been a prominent compound given its oxygen storage capacity and quite strong metal-support interactions that influence the chemical properties of metal particles supported on the CeO_2 surfaces.^{10–14}

Efficiency of these catalysts can be further improved, for instance, by lowering the temperature required for starting the CO oxidation. Several studies have focused on the lowering CO oxidation temperature, achieving regime of the so-called low temperature oxidation of CO (LTO CO).¹⁵ Pt is widely used as an active component of good LTO CO catalysts. When supported on CeO_2 , Pt can adopt such diverse structures as single atoms,^{16–20} small clusters,^{21–24} and nanoparticles.^{25,26} This structural diversity gave rise to other factors relevant for rationalizing the catalytic activity of Pt, for instance, the oxidation states of Pt atoms,^{27–30} CeO_2 surface facets,³¹ modification of the CeO_2 support by its doping^{32,33} or mixing with other oxides.^{34,35} Different parameters of the Pt/ CeO_2 nanomaterials define the Langmuir-Hinshelwood (LH) and Mars-van Krevelen (MvK) mechanisms commonly used to explain the CO oxidation catalytic activity.^{25,36,37}

Another feature of Pt deposited on ceria is that under oxidizing conditions, Pt particles can evolve to oxidized Pt species (PtO_x),^{38–43} which have demonstrated catalytic activity at temperatures as low as -40°C .^{42,44} The LH and MvK mechanisms discussed in the literature rely on quite high activation barriers for either the O-O bond breaking (LH) or the creation of a surface O oxygen vacancy in the support (MvK). For

instance, activation energies up to 0.9 eV²³ have been reported for the MvK mechanism, where kinetic studies showed significant catalytic activity well above room temperature.³⁷ Therefore, new mechanistic insights are required for rationalizing the high CO oxidation catalytic activity of PtO_x/CeO₂ nanomaterials at temperatures below 0°C.

In this work, density-functional theory (DFT) calculations and kinetic Monte Carlo (kMC) simulations are performed to evaluate the reactivity of Pt₆O₉/CeO₂ model catalyst towards CO and oxygen. Reaction mechanisms are proposed to rationalize activity of this catalytic system for CO oxidation at very low temperature. Several explored catalytic cycles show that when both the Pt₆O₉ cluster on CeO₂ and gas phase O₂ molecules provide O atoms for the CO oxidation, the involved activation energies become notably lower than those in alternative reaction mechanisms requiring taking O atoms from the CeO₂ support. According to the kMC results based on the present DFT data the proposed mechanisms are consistent with the CO oxidation catalytic activity at temperatures lower than 0°C.

Computational details

Computational methods

Spin polarized DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP).^{45–47} Valence electrons were described by plane wave basis set with a cutoff energy of 415 eV. The interaction between core and valence electrons was described using the projector augmented wave method (PAW).⁴⁸ The PAW potentials describe explicitly 2s and 2p electrons of C and O atoms, 5d and 6s electrons of Pt atoms and 5s, 5p, 6s, 5d and 4f electrons of Ce atoms. The PW91⁴⁹ generalized gradient approximation (GGA) functional was used adding a Hubbard-U⁵⁰ term for

Ce4f electrons, $U = 4.0$ eV,⁵¹ to better describe their localization underestimated by GGA.

Electronic structure convergence criterion was 5.0×10^{-6} eV and geometry optimizations were considered converged, when forces acting on atoms which were allowed to displace became smaller than 0.05 eV/Å. The climbing image nudge elastic band method (CI-NEB)⁵² is used to calculate transition state structures. The true character of the latter was confirmed by only one negative vibrational frequency, whereas all positive vibrational frequencies characterized every found local minimum structure.

Structural model

The Pt cluster used in this work is taken from ref. ⁵³, where Pt₆O₉ on CeO₂(111) surface (Fig. 1) was found to be the most favorable structure under slightly oxidizing conditions for all conceivable Pt₆O_x stoichiometries. The CeO₂(111) surface was represented by slabs with 2 O-Ce-O tri-layers, the thickness sufficient for the present study, and a 4×4 supercell with 12 Å of vacuum between neighboring slabs. For all DFT calculations, the O-Ce-O tri-layer in contact with the Pt₆O₉ cluster was allowed to relax while keeping the bottom tri-layer fixed in bulk positions with the optimized lattice parameter of 5.49 Å.

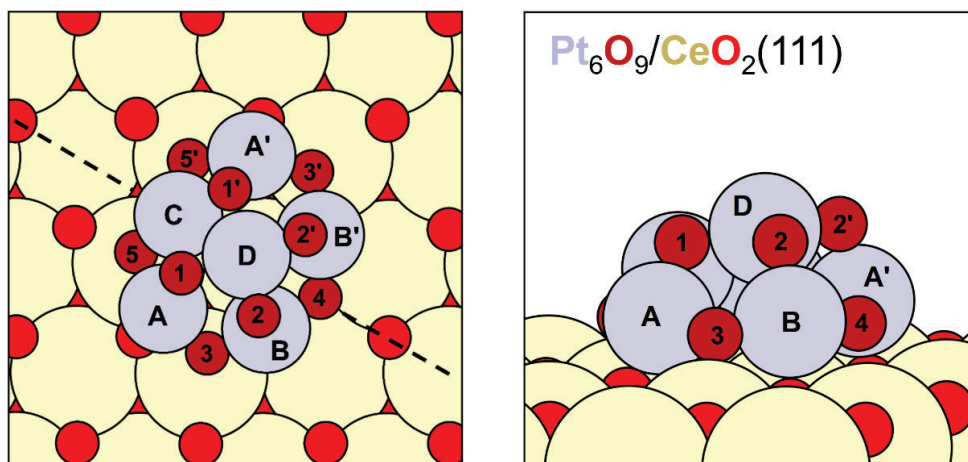


Figure 1: Globally optimized structure of Pt₆O₉ cluster supported on CeO₂(111) surface, ref. ⁵³: top view – left panel, side view – right panel. Color coding of atoms: Pt - grey, O of Pt₆O₉ – dark red, O of CeO₂ – light red, Ce – beige. Pt atoms of the Pt₆O₉ cluster are labeled with capital letters and its O atoms with digits. The dashed line displays a symmetry plane of the cluster, which makes the corresponding atoms with primed and not primed labels equivalent.

Kinetic simulations

Kinetic Monte Carlo simulations were performed using the first reaction method⁵⁴ as implemented in the MonteCoffee package.⁵⁵ The active sites of Pt on the Pt₆O₉ cluster were considered independent from each other, while constructing a list of neighbors that defines the connectivity of Pt atoms to surrounding O atoms and specifying events possible for a given site. The simulations were performed in the range -100 to 100 °C and 10 simulations were run for each temperature to ensure statistical accuracy.

Results and discussion

The reactivity of the Pt₆O₉ cluster on CeO₂(111) can be probed through the adsorption of CO on-top of different Pt atoms of the cluster. The resulting adsorption energies $E_{\text{ads}}(\text{CO})$, listed in Table 1, were calculated as follows:

$$E_{\text{ads}} = E(\text{CO}_{\text{top}}\text{-Pt}_6\text{O}_9/\text{CeO}_2) - E(\text{Pt}_6\text{O}_9/\text{CeO}_2) - E(\text{CO}),$$

where $E(\text{CO}_{\text{top}}\text{-Pt}_6\text{O}_9/\text{CeO}_2)$ and $E(\text{Pt}_6\text{O}_9/\text{CeO}_2)$ are the total energies of the CeO₂-supported Pt₆O₉ with and without CO adsorbed in on-top positions of Pt atoms, respectively. $E(\text{CO})$ is the total energy of the gas-phase CO molecule.

Pt atom	$E_{\text{ads}}(\text{CO})$, eV
C	-0.86
D	-0.83
A (A')	-0.69
B (B')	-0.19

Table 1: Adsorption energy $E_{\text{ads}}(\text{CO})$ of one CO molecule on-top sites of the different Pt atoms of the Pt_6O_9 cluster on $\text{CeO}_2(111)$ surface (see Figure 1 for labels of the Pt atoms). $E_{\text{ads}}(\text{CO})$ values for each pair of the primed and non-primed Pt atoms are equal.

Oxidation of the adsorbed CO molecule could precede using oxygen provided by the reducible CeO_2 support via the MvK mechanism.^{23,37} An alternative is to use for the oxidation oxygen atoms from the oxygen-rich Pt_6O_9 cluster. To this end, the O vacancy formation energy $E(\text{O}^v)$ for the Pt_6O_9 cluster on $\text{CeO}_2(111)$ was calculated to estimate the energetic propensity of the cluster oxygen atoms for CO oxidation (see Table 2).

O atom	$E(\text{O}^v)$, eV
2 (2')	1.71
1 (1')	1.76
5 (5')	1.92
4	2.17
3 (3')	2.23

Table 2: O vacancy formation energy $E(\text{O}^v)$ for the Pt_6O_9 cluster on $\text{CeO}_2(111)$ surface (see Figure 1 for labels of the O atoms). These values are notably lower than $E(\text{O}^v) = 3.02$ eV calculated for removal of a surface O atom of $\text{CeO}_2(111)$ closest to the Pt^{A} atom, which is representative of $E(\text{O}^v)$ values for the interface O sites of $\text{CeO}_2(111)$.

As seen in Figure 1, the O¹ and O² atoms have no direct bonds with the CeO₂ support. To differentiate them from the O³, O⁴ and O⁵ atoms forming bonds with the support, O¹ and O² atoms are called top layer ones, while O³, O⁴ and O⁵ are called bottom layer O atoms. Data in Table 2 show that top layer O atoms are energetically easier to remove than bottom layer O atoms and the vacancy formation energies in the cluster in general are smaller than in CeO₂(111) at the Pt₆O₉/CeO₂ interface.

Oxidation of the adsorbed CO molecule by O atoms of the Pt₆O₉ cluster is initiated by the interactions resulting in the O-CO complexes, whose formation energies are

$$\Delta E_f(\text{O-CO}) = E(\text{O-CO-Pt}_6\text{O}_9/\text{CeO}_2) - E(\text{CO}_{\text{top}}\text{-Pt}_6\text{O}_9/\text{CeO}_2),$$

where $E(\text{O-CO-Pt}_6\text{O}_9/\text{CeO}_2)$ is the total energy of the adsorbed O-CO complex on Pt₆O₉/CeO₂ and $E(\text{CO}_{\text{top}}\text{-Pt}_6\text{O}_9/\text{CeO}_2)$ is the total energy of CO adsorbed on top of a Pt atom in Pt₆O₉/CeO₂. Subsequent CO₂ desorption is characterized by the energy

$$\Delta E_{\text{des}}(\text{CO}_2) = E(\text{Pt}_6\text{O}_8(v\#)/\text{CeO}_2) + E(\text{CO}_2) - E(\text{O-CO-Pt}_6\text{O}_9/\text{CeO}_2),$$

where $E(\text{Pt}_6\text{O}_8(v\#)/\text{CeO}_2)$ is the total energy of the resulting Pt₆O₈/CeO₂ complex with $v\#$ specifying the O atom removed from the cluster by the desorbed CO₂ and $E(\text{CO}_2)$ is the total energy of the gas-phase CO₂ molecule. Several key O-CO and CO₂-desorbed structures were calculated along with the transition states to the O-CO structures. The $\Delta E_f(\text{O-CO})$, $E^\ddagger$ and $\Delta E_{\text{des}}(\text{CO}_2)$ values are shown in Table 3.

The formation of the O-CO complex is a favorable process stabilizing the system 1.0 to 1.8 eV. The energy barriers for this process are quite low, 0.1 - 0.5 eV. The subsequent CO₂ desorption is slightly endothermic or slightly exothermic, depending on the structure. The reactivity of Pt₆O₉ towards CO oxidation shows that overall, using Pt₆O₉ as the source of oxygen atoms, notably lower activation energies can be achieved compared to the 0.9 – 1.0 eV activation energies for metallic Pt particles.^{23,37}

O-CO/Pt	$\Delta E_f(\text{O-CO}), \text{ eV}$	$E^\ddagger, \text{ eV}$	$\Delta E_{\text{des}}(\text{CO}_2), \text{ eV}$
1A	-1.23	0.32	-0.30
1C	-1.15	0.45	-0.38
1D	-1.38	0.30	-0.14
2D	-1.82	0.52	0.24
3A	-1.24	0.10	0.19
5A	-1.03	0.43	-0.33
5C	-1.49	0.39	0.13

Table 3: Energies characterizing the activated O-CO complexes on $\text{Pt}_6\text{O}_9/\text{CeO}_2$. The O-CO/Pt sites are coded by the labels of the O atom reacting with CO and of the Pt atom, on which CO is adsorbed (see Figure 1). For instance, the notation 1A specifies that the O^1 and Pt^A atoms form this O-CO complex. $\Delta E_f(\text{O-CO})$ is the formation energy of O-CO/Pt from the on top adsorbed CO and O atom of Pt_6O_9 , $E^\ddagger$ is the activation energy for this reaction, and $\Delta E_{\text{des}}(\text{CO}_2)$ is the energy of CO_2 desorption with respect to O-CO/Pt.

The oxidation of the first CO molecule and CO_2 desorption results in the formation of a reduced $\text{Pt}_6\text{O}_8/\text{CeO}_2$ system, probably with a vacancy in the top layer O^1 atom site or the bottom layer O^3 atom site, since those are the sites with the lowest activation energies. Two further reaction paths starting from these structures are conceivable.

The first path is a re-oxidation of the cluster by the adsorption of an O_2 molecule at the vacancy site resulting in the Pt_6O_{10} cluster with an extra O atom for another CO oxidation reaction, following the reactant sequence $+\text{CO}/+\text{O}_2/+\text{CO}$.

The second path involves the adsorption of a CO molecule on the Pt_6O_8 cluster, further reduction to a Pt_6O_7 cluster after CO_2 desorption and re-oxidation to Pt_6O_9 by the adsorption

of an O₂ molecule in the last step, with a reactant sequence of +CO/+CO/+O₂. This reaction path will not be discussed.

In both paths, the adsorption of CO or O₂ on the sites around the newly created vacancy v1 or v3 are competitive processes. The adsorption energies for CO on the v1 and v3 vacancy sites are shown in Table 4. Adsorption energies $E_{\text{ads}}(\text{O}_2)$ of an O₂ molecule in the oxygen vacancies v1 and v3 of the Pt₆O₈ cluster are -1.67 eV and -1.84 eV, respectively.

Site	$E_{\text{ads}}(\text{CO})$, eV
Pt ^A v1	-1.26
Pt ^C v1	-0.64
Pt ^{2D} v1 ^a	-1.50
Pt ^C -Pt ^D v1	-1.50
Pt ^A v3	-2.39

Table 4: Adsorption energies $E_{\text{ads}}(\text{CO})$ of a CO molecule on Pt atom sites near O vacancy sites v1 or v3 of the Pt₆O₈ cluster formed after the first CO molecule oxidized.

The adsorption of O₂ on a O vacancy site is stronger than CO adsorption, except for CO on Pt^Av3, where quite strong adsorption can even lead to the site blocking (poisoning).

For the first reaction pathway proposed, CO adsorption energies are calculated for the Pt₆O₁₀(v1) and Pt₆O₁₀(v3) on Pt sites adjacent to the adsorbed O₂ molecule, considering also energy barriers for the formation of O-CO activated complexes and CO₂ desorption as displayed in Table 5. On the site Pt^Av3, the adsorption energy of CO is slightly smaller in magnitude than the activation energy for CO₂ formation on the same site. CO desorption and

CO₂ formation can be regarded as competitive events, while on the site Pt^Dv1 the activation energy for CO₂ formation is around 3 times smaller than that for CO desorption.

Site	E _{ads} (CO), eV	E [‡] , eV	ΔE _{des} (CO ₂), eV
Pt ^A v1	-0.49	0.76 ^a	-2.88
Pt ^C v1	-0.43	0.99 ^a	
Pt ^D v1	-0.51	0.17	-2.86
Pt ^A v3	-0.52	0.56 ^b	-3.16

a) The transition state structures characterizing these relatively high activation barriers were optimized with lower accuracy.

b) The transition state corresponds to the desorption of CO₂ instead of O-CO formation.

Table 5: Adsorption energies E_{ads}(CO) of CO on Pt sites of Pt₆O₁₀ near an O₂ molecule adsorbed in a vacancy site v1 or v3. E[‡] is the activation energy for the O-CO formation, ΔE_{des}(CO₂) is the energy of CO₂ desorption with respect to O-CO/Pt₆O₁₀.

With the desorption of the second CO₂ molecule and regeneration of the Pt₆O₉ cluster on CeO₂(111), a complete catalytic cycle is described with two different sets of elementary reactions that follow the same reactant sequence +CO/+O₂/+CO. Since these paths involve different O atoms from the cluster, we can refer to them as the top O layer cycle (Figure 2) and the bottom O layer cycle (Figure 3). The rate determining step (RDS) for the top layer cycle is the first CO₂ formation, with an energy barrier of 0.30 eV, while the second CO₂ formation has a barrier of 0.17 eV. For the bottom layer cycle, the first CO oxidation has a barrier of 0.19 eV while the second CO oxidation is the RDS with an energy barrier of 0.56 eV. Overall, the top layer cycle has a lower RDS and its barrier is around 3 times lower than the 0.9 – 1.0 eV activation energy reported for CO oxidation following the MvK mechanism on metallic Pt particles supported on CeO₂.^{23,37}

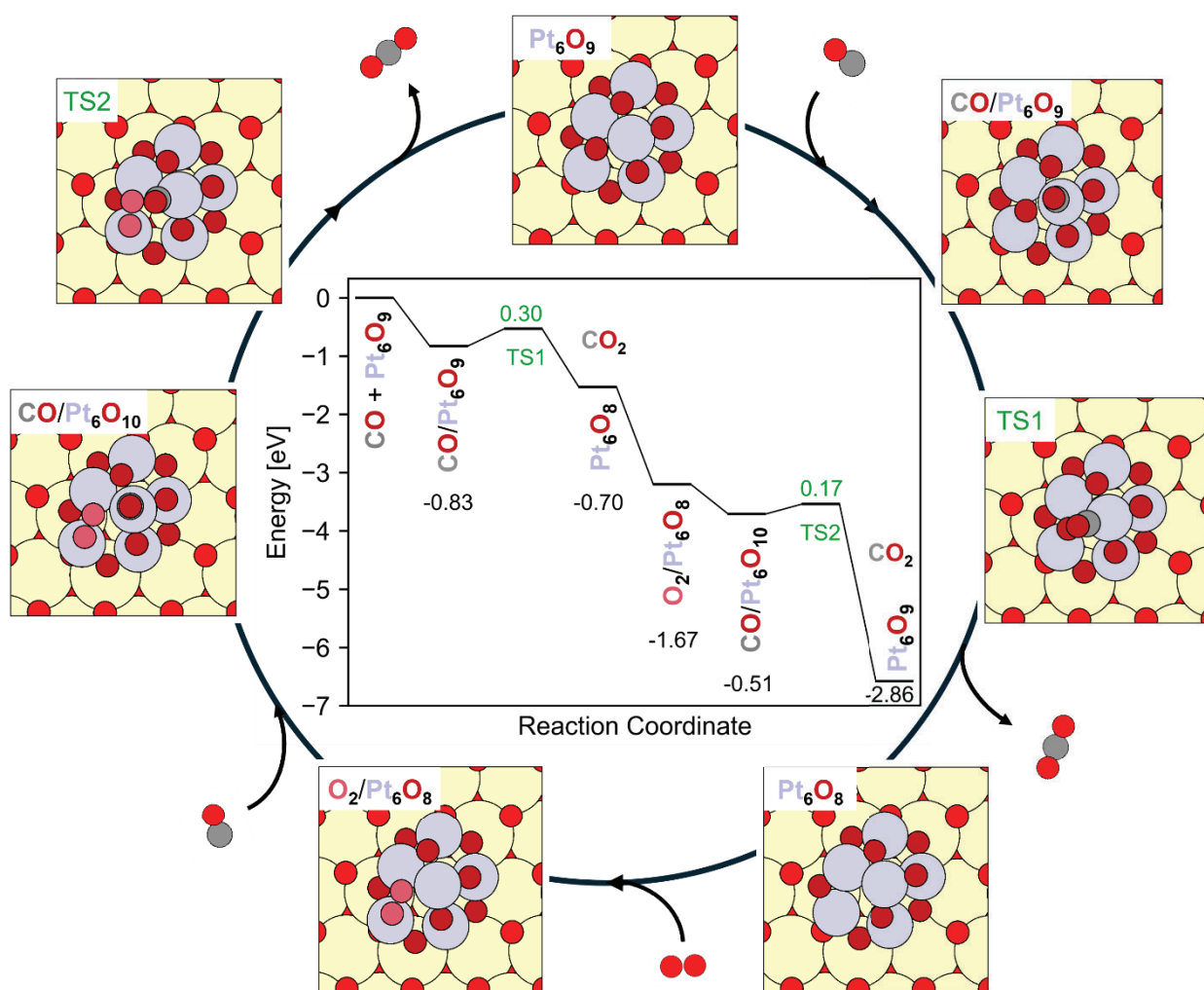


Figure 2: Potential energy diagram of the top layer catalytic cycle for CO oxidation, which involves O atoms from the top layer of the Pt₆O₉ cluster. The energy values shown in the diagram correspond to the change in energy with respect to the previous step in the reaction coordinate; the values in green are the activation energies.

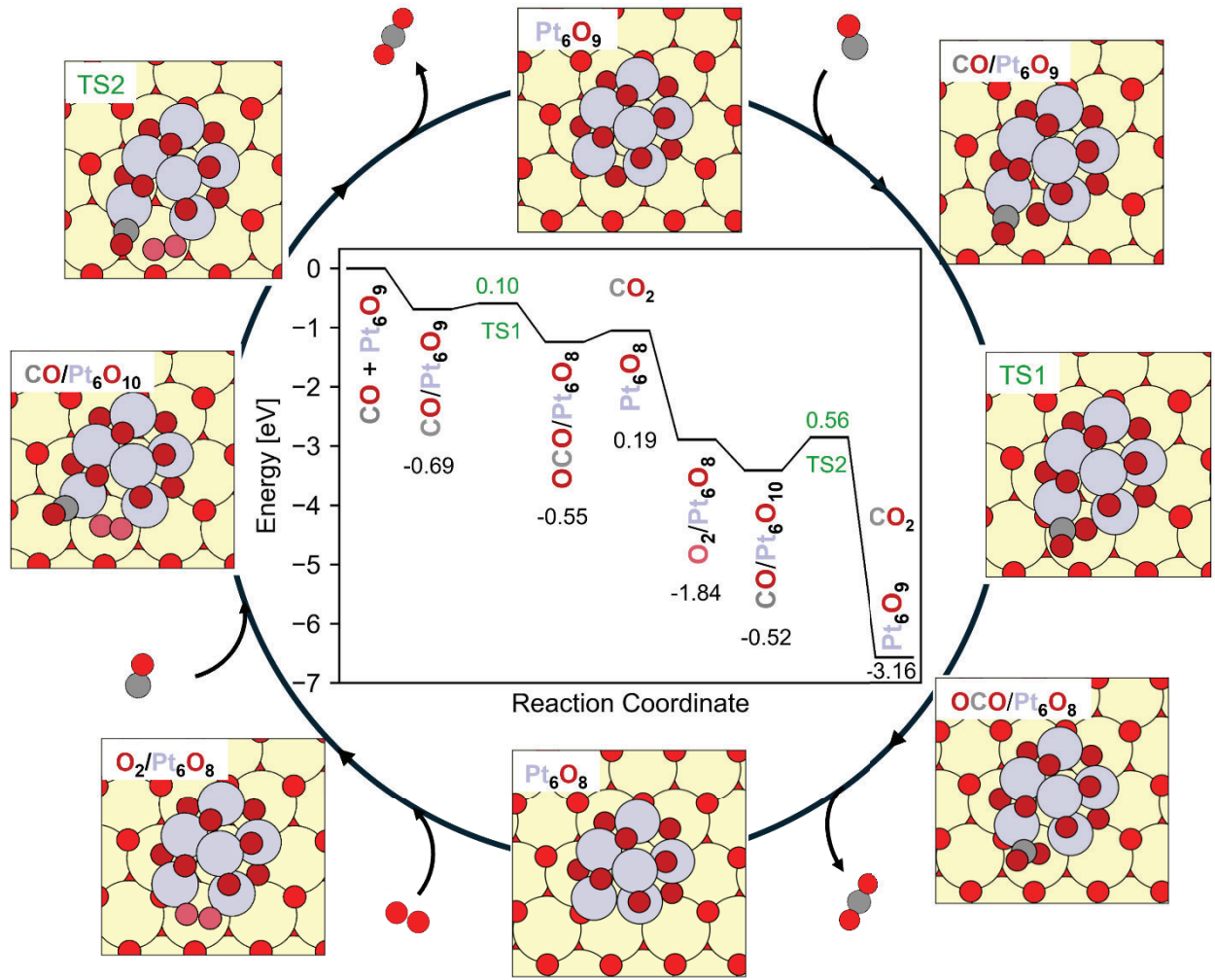


Figure 3: Potential energy diagram of bottom layer catalytic cycle for CO oxidation, involving O atoms from the bottom layer of the Pt₆O₉ cluster. The energy values shown in the diagram correspond to the change in energy with respect to the previous step in the reaction coordinate; the values in green are the activation energies.

Computational kinetic studies

The set of reactions described for the top layer and bottom layer catalytic cycles shown in Figures 2 and 3, along with their respective reaction energies and activation energies are used as input for the present kinetic Monte Carlo simulations. The considered reactions are:





Reactions R1-R5 represent each step of the catalytic cycles with a reactant sequence of CO/O₂/CO. The labels TL and BL describe the top layer and bottom layer catalytic cycles, respectively. R1 and R4 correspond to CO adsorption steps, R2 and R5 are CO₂ desorption steps with an intermediate step R2.5-BL in the case of the bottom layer cycle. R3 is O₂ adsorption on the vacancy site created by the CO₂ desorption from R2.

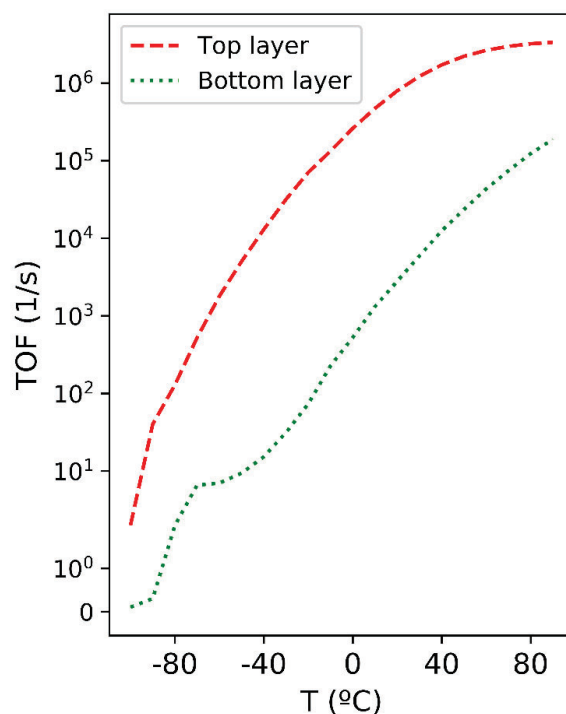


Figure 5: Calculated turnover frequency (TOF) values at different temperatures for the CO oxidation reaction described by the catalytic cycles shown in Figures 2 and 3: red line – top layer cycle, green line – bottom layer cycle.

The calculated turnover frequency (TOF) values are shown in Figure 5. For the top layer cycle the TOF at -40 °C is close to the value reported for the CO oxidation on metallic Pt particles supported on CeO₂ at ca. 100 °C.³⁷

The TOF values of the bottom layer cycle are consistently smaller by 2-3 orders of magnitude than the values of the top layer cycle in the temperature range -60°C to 60°C. Despite smaller activation energy for the first CO oxidation in the bottom layer cycle, the difference in energy of the RDS drives the kinetics of the process below room temperature.

Conclusions

CO oxidation reaction catalyzed by Pt₆O₉/CeO₂(111) model at very low temperatures was studied applying DFT calculations and computational kinetic simulations. The reactivity of the supported Pt₆O₉ cluster was addressed by considering CO adsorption and formation of oxygen vacancies in the cluster. The cluster features easily removable oxygen atoms with up to 1.3 eV smaller O vacancy formation energies than the vacancy formation energies in the CeO₂(111) slab at the interface with the Pt₆O₉ cluster.

Several reaction pathways are explored, where O atoms from the Pt₆O₉ cluster as well as gas phase O₂ are involved in the CO oxidation. These pathways involve CO activation by forming O-CO intermediates with O atoms from the cluster before CO₂ desorption with small activation energies ranging from 0.10 to 0.52 eV. Gas phase O₂ plays a dual role by healing the created O vacancies in the cluster and providing an extra O atom for the oxidation of a second CO molecule with the activation energies of 0.17 to 0.56 eV and thus completing a catalytic cycle.

The conceivable reaction mechanisms can proceed via two different catalytic cycles. The first cycle involves O atoms in the top layer of the Pt₆O₉ cluster with a rate determining step

characterized by the activation energy of 0.30 eV. The second cycle proceeds via O atoms from the bottom layer of the cluster, in contact with the CeO₂(111) support, and results in a rate determining step with the barrier of 0.56 eV.

The reaction energies and activation barriers obtained from DFT calculations for both catalytic cycles are used as parameters for kinetic Monte Carlo simulations to calculate TOF values for these catalytic cycles at very low temperatures. Results of these simulations show a high catalytic activity already at temperature as low as ca. -40°C. This finding is consistent with the experimental observations suggesting the low-temperature CO oxidation activity caused by interplay between supported Pt-oxide clusters and gas phase O₂, with the CeO₂ support being a spectator in these reaction mechanisms.

The insights gained in this work provide new mechanistic alternatives for designing efficient oxidation catalysts for reactions at very low temperatures based on supported metal oxide clusters not necessarily composed of scarce precious metals.

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Chapter 6: Conclusions

In the present doctoral thesis, computational simulations using DFT for different types of nanostructured catalysts supported on CeO₂ were studied. Their geometric and electronic structures along with their chemical properties have been evaluated, obtaining relevant insights about the nature of the interaction of different types of nanostructures with the CeO₂ support. The overall conclusions for the different types of nanostructures assessed are the following:

Metallic Pt clusters

- EMSI are observed due to the interaction between Pt₈ clusters and a reducible CeO₂(111) support. A systematic evaluation using Ce4*f*-core potentials revealed energy differences of up to 0.8 eV between electronic states differing in the number of Ce³⁺ and their positions in the CeO₂ surface with respect to the Pt₈ cluster. Systems with electrons transferred from Pt to CeO₂(111) were found to be ~0.5 eV more stable than those without transferred electrons.
- Interface Pt atoms of the Pt₈ cluster are the most impacted by EMSI. This impact is noticeable in the electronic structure, in terms of 5*d* orbital occupation and an inhomogeneous charge distribution of the supported Pt₈ cluster.
- EMSI have an important effect on the chemical properties of the supported Pt₈ cluster, as evidenced by the changes in adsorption energies of molecules such as H₂O and CO at interface adsorption sites of the Pt₈ cluster.
- The systematic use of Ce4*f*-core potentials was proven capable of characterizing various electronic states and their resulting electronic structure and charge distribution of the supported Pt₈ cluster.

FeO 2D-thin film

- The FeO(6x6)/CeO₂(5x5) model revealed a periodic corrugated structure, with areas displaced away from the CeO₂ support and other areas exhibiting Fe-O and O-Ce bonds at the oxide-oxide interface. This periodic structure was also observed by STM and LEED measurements.
- Dispersion forces play a key role in the formation of the FeO 2D thin film over the CeO₂ support. Around 45% of the formation energy of FeO/CeO₂ interface (-0.45 eV/FeO unit) comes from dispersion forces and makes the FeO thin film structure more favorable than

the formation of FeO bulk phase (-0.36 eV), indicating that the ceria-supported 2D structures are more stable than 3D FeO particles.

- Both models used show electron transfer from the FeO thin film to the CeO₂ support, in a process analogous to the EMSI, which is coined as EOSI. Computational models show a higher Fe²⁺/Fe³⁺ ratio (up to 3:1) than XPS measurements. Additional oxidation of the FeO 2D thin film by oxygen adsorption, forming Fe₄O₅ and Fe₄O₆ is a favorable process which could rationalize XPS results.
- Structural and electronic factors, such as structural corrugation, formation of Fe-O and Ce-O interfacial bonds, electron transfer, dispersion forces and additional oxidation explain the stability of a FeO 2D thin film supported on CeO₂.

Oxidized PtOx clusters

- The reactivity of Pt₆O₉ clusters supported on CeO₂ evaluated by vacancy formation energy shows that it can be up to 1.3 eV lower than for an O vacancy formation on the CeO₂ support.
- O atoms from the ceria-supported Pt₆O₉ cluster, as well as gas-phase O₂ are involved in a reaction pathway for CO oxidation where activation energies are between 0.19 and 0.52 eV.
- A new reaction mechanism for CO oxidation is proposed with the Pt₆O₉ being the active component and the CeO₂ support acting as a spectator, where the proposed reaction consumes 2 CO and 1 O₂ molecules to produce 2 CO₂ molecules.
- Two different catalytic cycles are described for the mechanism where O atoms are abstracted from either the top layer or the bottom layer of the Pt₆O₉ cluster. The top layer cycle and bottom layer cycle have a RDS with activation energies of 0.3 and 0.56 eV, respectively.
- With DFT values as inputs, kMC simulations reveal significant catalytic activity from -40°C. This suggests that low temperature CO oxidation is dependent on the presence of oxidative reaction conditions and a metal-oxide cluster structure as an active component.

Chapter 7: List of publications

- **Pablo Castro-Latorre**, Konstantin M. Neyman, Albert Bruix; *Systematic Characterization of Electronic Metal–Support Interactions in Ceria-Supported Pt Particles*. J. Phys. Chem. C 2023, 127, 36, 17700–17710
Contribution: Execution of all DFT calculations, preparation of figures and tables, draft writing and editing.
- Lesia Piliai, **Pablo Castro-Latorre**, František Pchálek, Shiva Oveysipoor, Yuliia Kosto, Ivan Khalakhan, Tomáš Skála, Konstantin M. Neyman, Pere Alemany, Michael Vorochta, Albert Bruix, Peter Matvija and Iva Matolínová; *Electronic and Structural Properties of Thin Iron Oxide Films on CeO₂*. ACS Appl. Mater. Interfaces 2024, 16, 35, 46858–46871
Contribution: Execution of all DFT calculations, elaboration of figures and draft review. Co-first author and PhD student Lesia Piliai (Charles University, Prague) carried out the experimental section of the publication, without participating in DFT calculations.
- **Pablo Castro-Latorre**, Henrik Grönbeck, Albert Bruix, Konstantin M. Neyman; *How Pt/CeO₂ Nanostructures Can Catalyze CO Oxidation at Very Low Temperature*. (To be submitted)
Contribution: Execution of all DFT calculations, preparation of figures and tables, kinetic monte carlo simulations and draft writing.

Other publications where the author contributed:

- Elena M. Slavinskaya, Andrey I. Stadnichenko, Jon E. Quinlivan Domínguez, Olga A. Stonkus, Mykhailo Vorokhta, Břetislav Šmíd, **Pablo Castro-Latorre**, Albert Bruix, Konstantin M. Neyman, Andrei I. Boronin; *States of Pt/CeO₂ catalysts for CO oxidation below room temperature*. J. Catal. 421 (2023) 285–299
Contribution: Execution of DFT calculations of fully reduced Pt particle supported on CeO₂ and its different electronic states, draft review.