Reactions of aqueous radiolysis products with oxide surfaces: 
An experimental and DFT study

Cláudio Miguel Lousada Patrício

AKADEMISK AVHANDLING
List of Papers

This thesis is based on the following papers:

I  "Kinetics, Mechanism, and Activation Energy of H₂O₂ Decomposition on the Surface of ZrO₂"

II  "Reactivity of H₂O₂ towards different UO₂-based materials: The relative Impact of Radiolysis Products Revisited"

III  "On the redox reactivity of doped UO₂ pellets-Influence of dopants on the H₂O₂ decomposition mechanism"


V  "Reactivity of metal oxide clusters with hydrogen peroxide and water – a DFT study evaluating the performance of different exchange–correlation functionals"

VI  "Enhanced hydrogen formation during the catalytic decomposition of H₂O₂ on metal oxide surfaces in the presence of HO radical scavengers”
Cláudio M. Lousada, Jay A. LaVerne, and Mats Jonsson, *Journal of Physical Chemistry C*, under review

VII  "Catalytic decomposition of hydrogen peroxide on transition metal and lanthanide oxides”
“Application of reactivity descriptors to the catalytic decomposition of hydrogen peroxide at oxide surfaces”
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My contributions to the papers:

Papers I, IV, VI: I did the experiments and most of the DFT calculations (IV) and wrote the first draft of the text.
Papers II: I did half of the experiments and wrote half of the first draft of the texts
Paper III: I did some of the experiments and wrote parts of the first drafts of the texts.
Paper VII: I did part of the experiments and wrote the first draft of the text.
Papers V, VIII: I did the DFT calculations and wrote the first draft of the text.
Abstract

The reactions between aqueous radiolysis products and oxide surfaces are important in nuclear technology in many ways. In solid-liquid systems, they affect (and at the same time are dependent on) both the solution chemistry and the stability of materials under the influence of ionizing radiation. The stability of surface oxides is a factor that determines the longevity of the materials where such oxides are formed. Additionally, the aqueous radiolysis products are responsible for corrosion and erosion of the materials.

In this study, the reactions between radiolysis products of water – mainly H\textsubscript{2}O\textsubscript{2} and HO radicals – with metal, lanthanide and actinide oxides are investigated. For this, experimental and computational chemistry methods are employed. For the experimental study of these systems it was necessary to implement new methodologies especially for the study of the reactive species – the HO radicals. Similarly, the computational study also required the development of models and benchmarking of methods. The experiments combined with the computational chemistry studies produced valuable kinetic, energetic and mechanistic data.

It is demonstrated here that the HO radicals are a primary product of the decomposition of H\textsubscript{2}O\textsubscript{2}. For all the materials, the catalytic decomposition of H\textsubscript{2}O\textsubscript{2} consists first of molecular adsorption onto the surfaces of the oxides. This step is followed by the cleavage of the O-O bond in H\textsubscript{2}O\textsubscript{2} to form HO radicals. The HO radicals are able to react further with the hydroxylated surfaces of the oxides to form water and a surface bound HO• center. The dynamics of formation of HO• vary widely for the different materials studied. These differences are also observed in the activation energies and kinetics for decomposition of H\textsubscript{2}O\textsubscript{2}. It is found further that the removal of HO• from the system where H\textsubscript{2}O\textsubscript{2} undergoes decomposition, by means of a scavenger, leads to the spontaneous formation of H\textsubscript{2}.

The combined theoretical-experimental methodology led to mechanistic understanding of the reactivity of the oxide materials towards H\textsubscript{2}O\textsubscript{2} and HO radicals. This reactivity can be expressed in terms of fundamental properties of the cations present in the oxides. Correlations were found between several properties of the metal cations present in the oxides and adsorption energies of H\textsubscript{2}O, adsorption energies of HO radicals and energy barriers for H\textsubscript{2}O\textsubscript{2} decomposition. This knowledge can aid in improving materials and processes important for nuclear technological systems, catalysis, and energy storage, and also help to better understand geochemical processes.
Sammanfattning

Inom kärnteknik är reaktioner mellan radiolysprodukter i vätskehela och metallytors oxider viktiga på många sätt. I fastfas-vätskehela-system påverkar de (och påverkas samtidigt av) både lösningens kemi och materialens stabilitet när de utsätts för joniserande strålning. Stabiliteten hos ytoxider är en faktor som delvis bestämmer materialens livslängd där sådana oxider bildas. Dessutom orsakar radiolysprodukter från vatten korrosion och erosion av materialen.

I denna studie undersöks de kemiska reaktionerna mellan vattenradiolysprodukter -främst H$_2$O$_2$ och HO radikaler- och metall-, lantanid- och aktinid-oxider. Studien omfattar båda experimentella och kvantkemiska beräknings- metoder. För de experimentella studierna av de här systemen behövdes nya metoder utvecklas och användas, särskilt för att studera de reaktiva HO radikalerna. Även för att utföra kvantkemiska beräkningar krävdes det utveckling av modeller och benchmarking av befintliga metoder. Experimenten, tillsammans med kvantkemiska beräkningar, producerade värdefulla kinetiska, energetiska och mekanistiska data.

Det är här bevisat att HO radikaler är en primär produkt från den katalytiska nedbrytningen av H$_2$O$_2$. För samtliga material sker den katalytiska sönderdelningen av H$_2$O$_2$ först genom molekylär adsorption på ytor av oxiderna. Detta steg följs av klyvning av väteperoxidens O-O bindning, vilket leder till bildning av HO radikal. HO radikalerna kan sedan reagera vidare med de hydroxylerade oxidernas ytor. Det leder till bildning av vatten och ett ytbundet HO•. Dynamiken för bildandet av HO• varierar betydligt för de olika material som studerats. Dessa skillnader observerades också i aktiveringsenergier och i kinetiken för sönderdelning av H$_2$O$_2$. Det visar sig vidare att när HO• avlägsnas -med hjälp av en radikalinfångare- från systemet där H$_2$O$_2$ genomgår nedbrytning bildas H$_2$ spontant.

Den kombinerade teoretiska-experimentella metodiken ger en mekanistisk förståelse av reaktiviteten av oxidmaterial gentemot H$_2$O$_2$ och HO radikaler. Denna reaktivitet kan uttryckas i termer av fundamentala egenskaper hos katjonerna som är närvarande i oxiderna. Korrelationer konstaterades finnas mellan flera egenskaper hos metallkatjoner närvarande i oxiderna och adsorptionsenergier för H$_2$O, adsorptionsenergier för HO radikaler och energibarriärer för H$_2$O$_2$s nedbrytning. Denna kunskap kan hjälpa till att förbättra material och processer som är viktiga för kärntekniska system, katalys och energilagring, och även bidra till att bättre förstå vissa geokemiska processer.
List of Abbreviations

DFT - Density functional theory
$G(x)$ - Radiation chemical yield for the species $x$
$\dot{C}(x)$ - Amount of species $x$ produced
$D$ - Radiation dose rate
$\rho$ - Solvent density
$k_2$ - Second-order rate constant
$k_1$ - First-order rate constant
$k_0$ - Zeroth-order rate constant
$k_c$ - Catalytic capacity of the surface
$S_a$ - Surface area of solid
$k$ - Reaction rate constant
$E_a$ - Arrhenius activation energy
$E_{a,ads}$ - Arrhenius activation energy of adsorption
$A$ - Arrhenius pre-exponential or frequency factor
$R$ - Gas constant
$T$ - Absolute temperature
$\Delta H^\ddagger$ - Enthalpy of activation
$k_B$ - Boltzmann constant
$h$ - Planck constant
$\Delta S^\ddagger$ - Entropy of activation
$\Delta G^\ddagger$ - Gibbs energy of activation
$\Delta G'$ - Gibbs free energy for the reaction
BEP - Brønsted, Evans and Polanyi
$\Delta E_{ads}$ - Adsorption energy
$\Delta H_{ads}$ - Adsorption enthalpy
$\alpha_{BEP}$ - Brønsted, Evans and Polanyi proportionality constant
AFM - Atomic force microscopy
SEM - Scanning electron microscopy
XRD - X-ray diffraction
UHV - Ultra-high vacuum
PW91 - Perdew-Wang functional
PBE - Perdew-Burke-Ernzerhof functional
GGA - Generalized gradient approach
MGGA - Meta-GGA
$\tau$ - Kinetic-energy density
HF - Hartree-Fock
LDA - Local density approximation
B3LYP - Becke, three-parameter, Lee-Yang-Parr functional
B3LYP-D - Becke, three-parameter, Lee-Yang-Parr functional supplemented with dispersion
B3LYP* - Becke, three-parameter, Lee-Yang-Parr functional with 15% Hartree-Fock exchange
PBE0 - Perdew-Burke-Ernzerhof functional supplemented with Hartree-Fock exchange
M06 - Minnesota 2006 functional
M06-L - Minnesota 2006 local functional
SIE - Self-interaction error
ECP - Effective core potential
GRD - Global reactivity descriptors
$\mu$ - Chemical potential
$E$ - Electronic energy
$N$ - Number of electrons
$Z$ - Atomic number
$\chi$ - Electronegativity
IP - Ionization potential
EA - Electron affinity
KS - Kohn-Sham
$\eta$ - Chemical hardness
HOMO - Highest occupied molecular orbital
LUMO - Lowest unoccupied molecular orbital
PBC - Periodic boundary conditions
SIMFUEL - Simulated high-burnup UO$_2$-based fuel
Tris - Tris(hydroxymethyl)aminomethane
TAPS - N-[Tris(hydroxymethyl)methyl]-3-aminopropanesulfonic acid
AAA - Acetoacatinilide
LACVP - Los Alamos effective core potential with split valence basis set 6-31+G(d)
* - Polarization functions
+ - Diffuse functions
$E_{HF}^{XC}$ - Hartree-Fock exchange
QST - Quadratic synchronous transit
CSDZ - Cundari-Stevens effective core potential basis set for lanthanides
$t$ - Time
$Sa/V$ - Solid surface area to solution volume ratio
BDE - Bond dissociation energy
B.E.T. - Brunauer, Emmet, and Teller
$P$ - Pressure
I.C.P. - Inductively coupled plasma spectroscopy
$b_2$ - Intercept at zero coordinate
EPR/ESR - Electron paramagnetic resonance/electron spin resonance spectroscopy
$\Delta E_r$ - Reaction electronic energy
CCSD(T) - Coupled-cluster with triple excitations allowed
PES - Potential energy surface
$D_{exp}$ - Absolute deviation from the experimental value for the activation energy
$E_a^{ZPE}$ - Activation energy with zero point energy correction
$S_{CA}$ - Surface catalytically active site
$K$ - Langmuir adsorption equilibrium constant
$X_m$ - Amount of adsorbate required for a monolayer coverage on the surface of an adsorbent
$k_a/k_d$ - Rate constants of adsorption/desorption
$C_e$ - Equilibrium concentration of adsorbate in solution
$e$ - Change in Mulliken charge
$\chi_P$ - Pauling electronegativity
$\lambda_{max}$ – Wavelength of maximum absorbance
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1. The context of this work

1.1 Chemical processes in nuclear technology

The chemistry of a nuclear reactor is a special topic in many ways. The extreme temperature and pressure at which nuclear reactors operate makes \textit{in situ} studies of their chemistry a difficult subject. In addition, very intense ionizing radiation is emitted from the reactor core. The materials that constitute a nuclear reactor have to withstand these extreme conditions and still be unsusceptible to unexpected failure. These features, which the public, operators and authorities expect from the materials present in a nuclear reactor, are to a very large extent controlled by the chemistry of the system. In general, the high temperature and pressure stability of the materials in nuclear reactors is extrapolated from laboratory data which are often obtained under conditions that are not as extreme as the ones in operating reactors.\(^1\) Though, the tools of thermodynamics make this approach possible and the materials stability can be predicted to a good extent from phase diagrams obtained under diverse conditions of temperature, pressure, concentration of solutes, ionic strengths of solutions, etc.

The fact that the materials surfaces suffer from wear and exhaustion in nuclear reactors is evident in deposits of corrosion products that appear in coolant circulation systems, valves, pumps, etc. These deposits, also called CRUD (Chalk River Unidentified Deposit), are the result of the materials wear and tear.\(^2\) They are a consequence of chemical processes and can affect the performance of the components where they build up deposits. Such deposits are very often radioactive, a feature which increases the occupational radiation exposure levels for technicians and other personnel.\(^3\) It is known that these deposits are corrosion products and as such are composed mostly of oxides of the metals that constitute the surfaces of the reactor. The stability of the reactor components surface oxides is a determinant factor for the longevity of the materials and the formation of deposits. The build-up of stable oxide layers leads to a decrease in the corrosion rate of the system surfaces.\(^4\) It is desirable that these oxides are as stable as possible in order to minimize the materials wear and erosion. The stability of the protective layers of oxides is dependent on a number of physical and chemical parameters such as pH, types of solutes present in the coolant, temperature, pressure, mechanical impact and radiation dose.\(^5\)

Even though thermodynamic stability data for reactor materials exist for a considerable range of: temperatures, pressures, solute concentrations and pH; at the atomic scale, little is known about the chemical processes occurring at the reactor materials surfaces.\(^6\) Initially there is the chemistry of the radiolysis products of water and solutes that leads to the formation of the oxide layers. This is mainly redox chemistry. After the formation of the
oxide, the chemistry changes and other types of reactions start to occur. The reactivity of the radiolysis products of water and the oxides surfaces involves more than pure redox chemistry. Instead, it becomes an ensemble of different chemical processes that affect the chemistry of the reactor and the stability of the protective oxides.

1.2 Interfacial processes in nuclear technology

The important processes in reactor chemistry described in section 1.1 are in water-cooled reactors, mainly solid-liquid processes. The build-up of an oxide layer occurs at the interface between the solid and the liquid phases. The chemistry of the interfacial processes is dependent on the properties of the solid material and of the liquid phase. The chemistry of a nuclear reactor is the result of a very large number of chemical reactions that occur in the liquid phase and at the interfaces between the liquid phase and the solid surfaces. The degree of complexity of this system is increased due to the presence of ionizing radiation and its interaction with the materials. This drives chemical phenomena that would not occur in the absence of ionizing radiation. Even though complex, this system can be understood by studying the key reactions that have a higher impact on the overall reactor chemistry.

The radiation chemistry of liquid water is a well-known phenomenon that had its main expansion in the middle of the twentieth century. The fast development in the knowledge of radiation chemistry of water was mainly due to the need of some developed nations to drive their nuclear programs. The fierce competition for the knowledge of radiation induced phenomena in water lead to the production of a large quantity of radiation chemical yields—so called G-values, rate constants for formation and reaction and stability constants for the radiolysis products of water. This knowledge lead to the development of other important fields of chemistry and many radiolytic species of water were studied thoroughly in solution. But even the most studied of those species, the solvated electron, still raises questions today, for example, in processes such as its interactions with organic molecules or other solutes besides pure water. With the development of the nuclear power technology, the deep knowledge of the radiolysis of water had proven to be of utmost importance for the understanding and control of the chemistry of reactors and to determine the stability of reactor materials under operation. Though, in spite of their importance for determining the stability of the materials and the reactor chemistry, the radiation induced processes occurring at the interfaces between the solid and the liquid phases remain scarcely understood. The existing knowledge on interfacial radiation chemistry processes is somewhat restrained to macroscale phenomena, such as the thermodynamic data for formation and stability of oxide layers, dissolution of corrosion products etc. These macroscopic processes are
though the result of microscale phenomena. This means, processes occurring at the atomic and molecular scale. To better understand and predict the macroscale observations, it is necessary to know what is happening at the microscale level that leads to a certain observable macroscale phenomenon. This will ultimately lead to a better control of chemical processes in nuclear technology, better understanding of the materials chemistry and aid in the development of improved materials for future usage in reactors and in nuclear waste management.

1.3 The scope of this work

It is the purpose of this work to bring knowledge to the field of radiation induced processes at solid-liquid interfaces. This means contributing to the understanding of the reactivity of radiolytic products of water and solid surfaces of relevance in nuclear technology. This knowledge is relevant not only for reactor technology applications but also for applications related with spent nuclear fuel, catalysis, and geochemistry or semi-conductor chemistry. It is the goal of this thesis to present and discuss studies which ultimately focus on the atomic and molecular scale understanding of solid-liquid interfacial processes. It is also the goal of this work to develop experimental and theoretical methodologies that can be used for future studies of such phenomena. Ultimately it is my wish to provide the materials scientists with information on chemical reactivity of metal oxides present in nuclear technological environments and to find correlations between properties of the materials and their reactivity towards a given radiolysis product.

2. Introduction

2.1 Water radiolysis

The interaction between ionizing radiation and matter, with this either in solid, liquid or gaseous state, leads to a multitude of physical and chemical phenomena. Water is no exception and its interaction with ionizing radiation leads to the formation of an array of chemical species with both diverse and interesting chemistry. Upon deposition of energy in a water molecule, it undergoes excitation to a higher energy level (i.e. electronic and/or vibrational and/or rotational). From there, one of two things can happen: the energy of the radiation is not enough to excite the water molecule to an electronic meta-stable state and the water molecule returns from the excited state to the ground state, releasing the excess energy as kinetic energy–radiant, translational, rotational or vibrational; the other outcome happens if the incident radiation is energetic enough to excite the water molecule to a meta-stable state where it will decompose into its
constituent species. The interaction of ionizing radiation with water leads to the second process, as the energy of this type of radiation is enough to transform the water molecule into its constituents which by means of further reactions form the so-called radiolytic products of water. Under a given dose rate, the amount of these products reaches a constant value, a steady-state concentration. The process of formation of the primary radiolysis products is complete in times in the order of $10^{-7}$ s after energy deposition. At this time, the products formed in a spur by the deposition of energy will have diffused away from the spur and the probability for their reactions with species formed in the same spur is negligible. Under these conditions, the water chemistry can be summarized by

$$\text{H}_2\text{O} \rightarrow e^-_{\text{aq}}, \text{H}^+, \text{HO}^-, \text{H}_2, \text{H}_2\text{O}_2, \text{H}_3\text{O}^+$$ \hspace{1cm} (R1)

The amount of products formed per unit of energy deposited is the radiation chemical yield or $G$-value. This is defined as the number of specified chemical events in an irradiated substance, produced per 100 eV of energy absorbed from ionizing radiation. The products of water radiolysis are well reported and their radiation chemical yields are known under a diversity of conditions. The $G$-value for a radiolysis product in a medium depends on the presence of solutes in that medium. The $G$-value is expressed in S.I. units as

$$G(x) = \frac{n_x}{\delta E}$$ \hspace{1cm} (1)

where $G(x)$ is the radiation chemical yield for the species $x$ and $n_x$ is the number of moles of $x$ formed per unit of energy ($\delta E$) in Joules (J) deposited in the medium. This definition of $G$-value applies for any solvent, but the $G$-value for a certain species is solvent dependent. In systems where only pure water is present, the time dependency of the events that lead to the formation of water radiolysis products can be represented by Figure 1.

**Figure 1.** Time scale of events in water radiolysis leading to the primary products.
The $G$-values for the primary $\gamma$-radiolysis products of water for the pH range 3 to 11 are

$$G(e_{aq}^-) = G(\text{HO}^\cdot) = G(H_2O^+) = 2.7 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$$

$$G(H^\cdot) = 0.6, \quad G(H_2) = 0.45, \quad G(H_2O_2) = 0.7 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$$

the $G$-values for a given radiolysis product can be used to obtain its concentration as a function of the time dependent energy deposition through

$$\dot{C}(x) = G \dot{D} \rho$$

where $\dot{C}(x)$ is the amount of the species $x$ produced in mol $\cdot$ dm$^{-3}$ $\cdot$ s$^{-1}$, $\dot{D}$ is the radiation dose rate, and $\rho$ is the solvent density. The concentration of a radiolysis product can be controlled by adding a reactant to the media that reacts with the precursors of that radiolysis product which will lead to a different $G$-value. As an example, the $G$-value for the HO radical in pure water is $2.7 \times 10^{-7}$ mol $\cdot$ J$^{-1}$. In a solution saturated with N$_2$O, the following reactions will take place

$$e_{aq}^- + N_2O \rightarrow N_2 + 0^\cdot$$  \hspace{1cm} k = 9.1 \times 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \quad (R2)$$

$$0^{\cdot\cdot} + H_2O \rightarrow \text{HO}^\cdot + \text{HO}^\cdot$$  \hspace{1cm} k = 1.8 \times 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \quad (R3)$$

where $k$ is the rate constant for the respective reaction. Under these conditions, the $G$-value for HO$^\cdot$ becomes $5.5 \times 10^{-7}$ mol $\cdot$ J$^{-1}$. Under reactor conditions, similar changes in $G$-values of radiolysis products occur when additives are added to control the reactor chemistry. For example the addition of H$_2$ to a reactor coolant is done in order to mitigate the formation of oxidative water radiolysis products such as H$_2$O$_2$ and O$_2$ and leads to the following reactions

$$H_2 + \text{HO}^\cdot \rightarrow H_2O + H^\cdot$$  \hspace{1cm} (R4)$$

$$H^\cdot + H_2O_2 \rightarrow H_2O + \text{HO}^\cdot$$  \hspace{1cm} (R5)$$

H$_2$O$_2$ and HO$^\cdot$ are precursors of O$_2$ according to

$$\text{HO}^\cdot + H_2O_2 \rightarrow \text{HO}_2^\cdot + H_2O$$  \hspace{1cm} (R6)$$

$$\text{HO}_2^\cdot + \text{HO}_2^\cdot \rightarrow O_2 + H_2O_2$$  \hspace{1cm} (R7)$$

In the presence of an excess H$_2$, the O$_2$ concentration is reduced following

$$H^\cdot + O_2 \rightarrow \text{HO}_2^\cdot$$  \hspace{1cm} (R8)$$

The decrease in H$_2$O$_2$ concentration is explained with the fact that the overall rate of the reactions that destroy H$_2$O$_2$ are increased. Even though other species are more powerful oxidants, such as the HO radical, these are usually short lived and the time necessary for their diffusion until they reach a surface will be longer than their half-life in solution. The HO radical
contribution to the oxidative power of the radiolysis products of water is then much less than that of H$_2$O$_2$ which is a long lived species in comparison. H$_2$O$_2$ is the most important molecular oxidant from the radiolysis products of water.

### 2.2 Chemical kinetics and transition state theory

It is known that some processes that lead to a lower energy state of a chemical system take place readily. Though, the majority of chemical reactions, even though they lead to a decrease in the systems energy upon formation of products, have a rate which in many cases is low. One of the features regarding the study of reaction rates is that with the exception of very specific simple systems which are far from real – laboratory sized – systems, a rate cannot be calculated from first principles. Theory is not yet developed to the point where it is possible to calculate how fast most reactions will take place, with the exception of some simple reactions. Though, for complex systems, obtaining kinetic parameters from first-principles is still a field in development. Chemical kinetics is then, largely, an experimental science. Under reactor conditions, the kinetics determines the steady-state concentrations of radiolysis products. Even though the reactions of the very reactive radicals formed according to (R1) are thermodynamically favorable, these radicals exist in steady-state concentrations under a constant dose rate of radiation. This is because at steady-state conditions the rates of their formation are equal to the rates of their consumption.

For some reactions, in a wide range of concentrations, the rate law is independent of the concentration of reactant. An example of this is the decomposition of a reactant on the surface of a catalyst. The reaction takes place on the catalytically active sites of the surface of the catalyst. This happens because the reactant is adsorbed to the surface and, within a range of reactant concentrations and catalyst surface areas the catalyst surface becomes essentially saturated with reactant. As such, the total concentration of reactant in solution does not influence the surface processes as long as there is enough reactant to cover the active sites on the surface of the catalyst. Consequently, the decomposition of a reactant on a specific, fixed amount of catalyst occurs at a constant rate over a wide range of reactant concentrations. This is no longer valid as the reaction approaches completion. Under such conditions, the concentration of reactant does affect the rate of the reaction because its concentration determines the rate at which the active sites on the solid surface become occupied. For conditions where the reaction rate is independent of the reactant concentration, the reaction is zeroth-order with respect to that reactant.
For a heterogeneous reaction – such as the case of a solute $R$ reacting with an aqueous particle suspension of a solid – which obeys first-order kinetics, the second-order rate constant can be determined by studying the variation in the first-order rate constant as a function of solid surface area to solution volume ratio. The second-order rate expression is given by

$$-\frac{d[R]}{dt} = k_2 \left( \frac{Sa}{V} \right) [R]$$

where $Sa$ denotes the surface area of the solid, $V$ is the volume of the solution where the reaction takes place and $k_2$ is the second-order rate constant. For the case where the reaction obeys zeroth-order, its catalyst surface area dependency gives a quantity which represents the catalytic capacity of the surface and is expressed in the units of mol·m$^{-2}$·s$^{-1}$.

The transition-state theory initially formulated by Eyring in 1935, and its further developments provide tools to extract energetic data from kinetic parameters. The transition state theory allowed for a major breakthrough in the understanding of chemical reactivity because it is based in the premise that thermodynamic data can be obtained from kinetic data. And in turn the kinetic parameters of chemical reactions depend on thermodynamic properties of the system such as the activation enthalpy and entropy. Though, prior to this less empirical treatment of the effect of temperature in the reaction rates, an empirical approach to extract energetic data from reaction kinetics had been developed by Svante Arrhenius. His equation relates the temperature dependency of the rate constant of a reaction with the reaction activation energy according to

$$k = A e^{-\frac{E_a}{RT}}$$

where $k$ is the reaction rate constant, $R$ is the gas constant, $T$ is the absolute temperature, $E_a$ is the Arrhenius activation energy and $A$ is the pre-exponential or frequency factor. Following the Arrhenius approach and applying concepts from thermodynamics, kinetic theory and statistical thermodynamics, Eyring developed the concepts of the transition-state theory which relates the temperature dependency of a reaction rate with thermodynamic quantities according to

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

or,

$$k = \left( \frac{k_B T}{h} \right) e^{\left( \frac{\Delta S^\ddagger}{R} \right)} e^{\left( -\frac{\Delta H^\ddagger}{RT} \right)}$$

where $k$ is the reaction rate constant, $T$ is the absolute temperature, $\Delta H^\ddagger$ is the enthalpy of activation, $R$ is the gas constant, $k_B$ is the Boltzmann constant, $h$ is the Planck constant and $\Delta S^\ddagger$ is the entropy of activation and $\Delta G^\ddagger$ is the Gibbs energy of activation. Although the significance of the quantities $A$ and $E_a$ extracted from equations (4) and (5) have been debated since many years, at $T = 298.15$ K, $\Delta H^\ddagger$ is lower than $E_a$ by $2.5$ kJ·mol$^{-1}$ according to
2 Introduction

\[ \Delta H^+ = E_a + RT \]  \hspace{1cm} (6)

In a similar way, the Arrhenius quantity \( A \) relates with \( \Delta S^+ \) according to

\[ A = \frac{k_B T}{h} e^{(1+\Delta S^+/R)} \]  \hspace{1cm} (7)

The application of the equations (4) and (5) to kinetic data can produce valuable mechanistic information. For example, the rigidity of the path from the reactant to the transition-states for the same reaction occurring at two different catalyst surface sites can be better understood by comparing the obtained quantities \( \Delta S^+ \) for the reactions, provided that both reaction rates obey the same rate law.

2.3 Surface reactions and catalysis

The typical processes of a surface reaction involving a solute and a solid phase are represented in Figure 2.

![Figure 2](image)

Figure 2. Stages of a surface reaction. \( R_{sol} \) and \( R_{ads} \) represent the reactant in solution and adsorbed onto the surface respectively. \( TS_{ads} \) represents the transition state for the reaction occurring at the surface. \( P_{ads} \) and \( P_{sol} \) represent the reaction products adsorbed and in solution. \( k_{ads} \), \( k_{sr} \) and \( k_{des} \) are the rate constants for the adsorption, surface reaction and desorption respectively.

For a catalytic process, the surface will suffer none or only negligible alterations during those stages. While for a non-catalytic process, the surface will suffer alterations such as corrosion, surface dissolution, poisoning, formation of complexes, etc. If the path taken by the reactant is followed from the initial stage where the reactant is free in solution, until the products are released from the surface into solution, there are several steps such as: diffusion to the interface, adsorption onto the surface followed by the surface reaction which can itself consist of several steps, and desorption of products into solution. Each of these transformations will have an energy cost associated and as such these steps can have different rates. The kinetic study
of surface processes such as the one represented in Figure 2 poses a challenge in the sense that each of these steps have to occur on time scales different enough in order for the obtained kinetic data to correspond to the process of interest. This is not always possible and the study of surface reaction kinetics is a multidisciplinary field in what concerns the strategies used to study the individual processes represented above.\textsuperscript{20,21}

The concept of catalysis was introduced by Jöns Jacob Berzelius in the early 1800s to describe a number of phenomena that had been practiced prior to his definition. The special feature of a catalyst is that it lowers the energy cost necessary for a chemical transformation to occur. An example is shown in Figure 3.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{potential_energy_surface.png}
\caption{Potential energy surface for a non-catalyzed reaction (higher line) and for a surface catalyzed reaction (lower dashed line). $E_a$ – activation energy for the reaction. $\Delta G^\circ$ – Gibbs free energy for the reaction.}
\end{figure}

The potential energy surface shown for the catalyzed reaction usually consists of a series of processes that differ from the non-catalyzed reaction pathway. In the case of a surface reaction, there might exist several energy barriers associated with each of the processes represented in Figure 2. Even if this is the case, the activation energy for the catalyzed reaction will be less than for the case of the non-catalyzed process. The rate of a reaction is inversely proportional to the height of its activation energy and this means that the catalyzed reaction proceeds faster.

Molecular diffusion is a function of temperature, solvent viscosity and size of the molecule undergoing diffusion. For small molecules within the approximate size range of water molecules, when the solvent is water, the energy barrier for diffusion in the bulk is usually very low or even nonexistent. For some cases where temperature-induced enhancement of the local viscosity causes anisotropy in solvent micro-solvation mechanisms
which leads to changes in the micro-viscosity, Arrhenius activation energy barriers such as 33 kJ·mol\(^{-1}\) have been reported for a species to diffuse through such media.\(^\text{22}\) The residence time in a solvation sphere, for a small mass molecule capable of hydrogen bonding with water, such as H\(_2\)O\(_2\), is very short, in the order of 2.5 ps.\(^\text{23}\) This means that the diffusion of a H\(_2\)O\(_2\) molecule in liquid water is a process almost as fast as the diffusion of a water molecule and occurs with a negligible energy cost associated. For the majority of the surface reactions of H\(_2\)O\(_2\) at room temperature, this process – i.e. diffusion in the bulk solvent or in the regions adjacent to the interface with a solid – will not be the rate determining step.

When immersed in a solvent, surfaces undergo solvation just like a solute. The major difference is that the surface causes a discontinuity of the solvent media and unlike a solute creates a potential energy barrier for the mobility of the solvent molecules. This leads to the formation of an interface between the solid surface and the solvent. An interface is a special region where the solvent molecules have a different disposition from the bulk solution. This disposition will be determined by the Coulomb interactions between the surface and solvent molecules. Recently, it has been demonstrated that for a hydrophobic surface, as the resultant interaction with water is repulsive, at the interface, the solvent density is lower than in the bulk.\(^\text{24-28}\) For a hydrophilic surface, the Coulomb attraction between solvent water and surface increases the density of the water at the interface.\(^\text{28}\) Both situations are dependent on the density of polar groups at the surface. It has been shown that at an interface with a diamond surface, the water density can increase up to 2.5 kg·L\(^{-1}\). Also, in this region, the viscosity is higher and the mobility of a solute will be lower than in the bulk and a barrier for its diffusion might develop at such interfaces. In the solvent region close to the interface with a surface, the mass transfer resistance depends on the barrier for diffusion posed by slow-moving solvent adjacent to that interface.\(^\text{29}\) As the metal oxide surfaces of interest for this study are mostly hydrophilic,\(^\text{30}\) the discussion of interfaces from this point on will refer to hydrophilic surfaces unless otherwise stated.

In most cases the wetting of surfaces implies adsorption of water molecules.\(^\text{31,32}\) The adsorption of water onto surfaces can be divided into two types depending on the transformation that the water molecules undergo upon adsorption. Dissociative adsorption of water means that the water molecule undergoes splitting into H\(^+\) and HO\(^-\) upon adsorption. These products will bind to the nucleophilic and electrophilic surface sites respectively. In a metal oxide, the nucleophilic sites will usually be the exposed surface O anions while the electrophilic sites will be the surface exposed metal cations.\(^\text{30}\) This type of adsorbed water constitutes the adsorption layer closer to the surface and it is often the most exothermic
mode of adsorption of water. When moving from the surface towards the bulk media, the water which is adsorbed to the surface and it is not split into its constituents is molecularly adsorbed. The mobility of these water layers increases as going away from the surface towards the bulk solution. An example of this can be seen in Figure 4 for water adsorbed onto the surface of TiO$_2$.

![Figure 4](image-url.jpg)

**Figure 4.** Water on TiO$_2$ surface. Surface water molecules (O atoms in red, green, and blue, H in white) on a catalytically active nanomaterial (dots under the water molecules). Image: courtesy of Oak Ridge National Laboratory, Tennessee, USA.

The rigidity of the layers of water molecules shown in Figure 4 is higher for the green water molecules followed by the blue labeled layer. The least rigid is the layer labeled in red. Layers further from the surface will have more resemblance with the bulk solvent. At the layers closer to the surface, the water structure usually resembles that of ice in what concerns its mobility, even though it shows a different arrangement in terms of bonding angles and structure.$^{33,34}$ The processes involved in the diffusion of a reactant from the bulk liquid until it adsorbs onto the surface, are thus very different from gas-solid processes. At the water-solid interface, the surface adsorbed water layers have an important role in determining the reactivity of the surface.$^{35}$ Because this will affect phenomena such as: involvement of the dissociatively adsorbed water on the reaction mechanisms, energy transfer from adsorbates onto the surface upon impact; surface sideways diffusion of adsorbates, hydrogen atom transfer mechanisms, surface reconstruction upon water adsorption, etc. The energy cost for sideways diffusion of adsorbates will usually be higher for a solvated surface than for a gas-phase exposed surface.$^{36}$
Adsorption is a process that consists of chemical interactions between an adsorbate and a surface. These interactions can be of several types, ranging from van der Waals type, to covalent or ionic bonding.\textsuperscript{37} Depending on the type of interaction between adsorbate and substrate, adsorption is usually categorized into two kinds: chemisorption or physisorption. According to IUPAC: "The problem of distinguishing between chemisorption and physisorption is basically the same as that of distinguishing between chemical and physical interaction in general." Even though difficult to distinguish clearly, some aspects of each of these types of adsorption are characteristic and a distinction can be made to some extent. In physisorption, the forces involved are weaker than in chemisorption. These are usually intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and which do not involve a significant change in the electronic orbital patterns of the species involved. This type of bonding is rather weak. In chemisorption, bonds of the same kind as those that lead to the formation of chemical compounds such as covalent and ionic, are usually involved. This type of adsorption has chemical specificity and it is a process that usually has an activation energy associated. In the chemisorption process, the overlap of the wave functions of adsorbate and substrate is large and changes in the electronic structure of adsorbate and substrate can be observed. In this case, the molecular orbitals of the adsorbate interact with the substrate to produce a new set of electronic levels. Also according to IUPAC: "No absolutely sharp distinction can be made and intermediate cases exist, for example, adsorption involving strong hydrogen bonds or weak charge transfer." Nevertheless, in literature, authors describe chemisorption as a type of adsorption that involves bonding stronger than 50 kJ·mol\textsuperscript{-1} and physisorption as involving bonding weaker than 10 kJ·mol\textsuperscript{-1}.\textsuperscript{38} Other authors consider the physisorption energies to lay around 30 kJ·mol\textsuperscript{-1}.\textsuperscript{39} This kind of nomenclature is somehow ambiguous and does not provide a clear description of the adsorption process. A more consistent and less ambiguous nomenclature is that of molecular and dissociative adsorption. As the names indicate, molecular adsorption is the type of interaction where upon adsorption onto a surface, the adsorbate does not suffer intramolecular bond breaking – \textit{e.g.} water molecules in Figure 4. In turn, upon dissociative adsorption the adsorbate undergoes intramolecular bond breaking and new chemical species are formed – \textit{e.g.} first layer of water adsorbed onto a TiO$_2$ (110) surface.\textsuperscript{40} Adsorption of an adsorbate onto a surface will also have an impact on the surface structure. Surface reconstruction will very often occur upon adsorption. The extent of this reconstruction will depend on the strength of the chemical bonding between the surface and the adsorbate, as well as on the stability of the surface.\textsuperscript{37} The pH has also an important effect in the adsorption processes occurring at surfaces in solution. At pH values
lower than the point of zero charge, metal oxide and hydroxide surfaces are positively charged, with an excess of protons bound to the surface. Thus, these surfaces tend to repel positively charged ions and attract negatively charged ions. In the specific case of the systems studied in this work, this can trigger the formation of more stable hydrogen-bonded clusters of hydrogen peroxide in solution and on the surface, having the effect of stabilizing the hydrogen peroxide. At the pH of the point of zero charge, the surface becomes charge neutral and electrostatic repulsion of a positively or negatively charged ion is minimized. At pH above the point of zero charge, the surface becomes negatively charged because of the predominance of hydroxo (OH\(^-\)) or oxo (O\(^2^-\)) groups on the surface. Under these conditions, a positively charged ion in solution is attracted to the surface, while a negatively charged ion is repelled.

In general terms, the reactivity of surfaces is determined by the type of chemical elements that constitute the surfaces and by their chemical connectivity and environment. The stability and reactivity of a surface adsorbed species is determined by the type of its bonding with the surface. If the interactions with the surface are strong enough, the adsorbate bonds suffer changes such as elongations and bond breaking in the adsorbate can occur. For the interactions between the adsorbate and surface to occur, new molecular orbitals are formed and the resulting interaction energy is determined by the distribution of electrons over the bonding and anti-bonding orbitals that form the bonds with the surface. The shape and energy of these newly formed molecular orbitals and their occupancy will determine the reactivity of the system surface-adsorbate. Consequently, the type of adsorption is an important factor for determining the reactivity of the adsorbed molecule.

The adsorption structures – i.e. if the molecule adsorbs atop, bridging or in higher coordination – relates to the effects that determine the structures and energies of transition-states of reacting surface species. As such, being able to foresee the interactions that are determined by the adsorption complexes is a long term goal of surface chemists because this would mean to have a clearer idea of the transition-state structures and of the reactivity of the adsorbed complex. For a homologous series of reactions, Brønsted, Evans and Polanyi (BEP) demonstrated that there is a linear correlation between the transition state energies and the adsorption energies. This is because for a homologous series, the changes in activation energies and the changes in adsorption energies are governed by the same physical principles. That correlation is simply explained by
where $E_a$ is the activation energy, $\Delta E_{ads}$ is the adsorption energy of the reactant, and $\alpha_{BEP}$ is the proportionality constant. When $\alpha_{BEP} < \frac{1}{2}$ the transition state is said to occur early. When $\alpha_{BEP} > \frac{1}{2}$ the transition-state structure is considered to occur late.

All these processes depend on the connectivity between the adsorbate and the surface. Here the important role that surface defects have in the chemical bonding and reactivity of adsorbates has to be considered. This has been demonstrated by experimental and theoretical studies.\(^4^8\) It was shown for example that the reaction of water with MgO(100) surface occurs only at defect sites. Also, correlations between defect density on the surface of metal oxides and their reactivity have been reported.\(^4^9\) The reactivity of such surface defects can be orders of magnitude higher than the reactivity of non-defective surface sites. As such, it is expected that those surface defects play a decisive role in surface reactivity. The effect of defects on surface reactivity can have structure specificity. This means that specific types of surface defects are able to selectively catalyze certain types of reactions.\(^5^0\) This is because the binding of adsorbates and reaction products to the different surface defects will be different and might involve different orbitals from the surface atoms.

While it is thought that such defects may dominate interfacial reactivity, little is known about the nature and density of such features on real particles. This is because such studies are challenging in the sense that the techniques that can be applied to surface structure studies are either very local \textit{i.e.} AFM, SEM, etc; or global \textit{i.e.} confocal profilometry, XRD, etc. The techniques based on electron scattering and their derivatives, produce results that are a weighted average of the contribution of the most common surface sites. Let us consider a surface defect which is 1000 times more reactive than a non-defective surface site. Let us suppose that only 1\% of the total surface is constituted by such defects.\(^5^1\) When running an electron diffraction based technique (for example) to study this surface, the defective site will not be visible, but it might still be the surface site that governs the overall surface reactivity.

Surface science studies are usually performed under controlled conditions using surfaces which are homogeneous in terms of their chemical composition and structure.\(^5^2\) However, such surfaces exist only in ultra-high vacuum (UHV). The results of these studies are not generally applicable to real interfacial systems – \textit{i.e.} systems where surfaces are in contact with liquids, fluids, gases, organic matter, etc. Real surfaces have structures and reactivity that may be affected by interactions with the environment. Even when only liquid water is present it will affect the geometric and/or
electronic structures of surfaces and those surfaces will not be the same as under UHV conditions.

2.4 Density functional theory

Note: for a more detailed explanation of some concepts involved in DFT see Section 7 of this thesis.

Within the framework of DFT, two of the most widely used density functionals in calculations involving solids are the Perdew-Wang functional (PW91) and the Perdew-Burke-Ernzerhof functional (PBE). The PBE is a parameter free functional which was constructed by making the functional form to satisfy some constraints. Though, these general gradient approach (GGA) type of functionals, in spite of producing good adsorption energies, deviate considerably from experiments in what concerns the description of open shell systems and description of energy barriers for reactions. The improved GGA’s, the meta-GGA’s (MGGA) take into account the second derivative of the electron density, i.e., the Laplacian. Due to difficulties in calculating numerical results for the Laplacian, an alternative MGGA formalism that is more numerically stable is to include in the exchange-correlation potential a dependence on the kinetic-energy density ($\tau$). The cost of a calculation using a MGGA functional is similar to that for a GGA calculation, and the former is typically more accurate than the latter for a pure density functional. Also, the MGGA’s perform better than the GGA’s in describing non-covalent interactions.

In order to correct the deviations of both the local density (LDA) and GGA based functionals from the Hartree-Fock (HF) results, new functionals were developed which include HF exchange. These functionals involve DFT correlation with a combination of DFT and HF exchange. This class of functionals is designated by hybrid functionals. In the design of hybrid functionals, the optimal amount of HF exchange to include in the functional is either chosen to assume a specific value – between 0 and 100% – or is obtained by fitting: in a way that the resulting functional performs the best in predicting the properties of a molecular database. The B3LYP functional was designed in such a way. It was optimized to reproduce geometries and binding energies of molecular systems to the same accuracy as low-level post-Hartree-Fock methods with the advantage of a significantly lower computational cost. B3LYP can provide accurate molecular geometries even when hydrogen bonds are present. The other approach, that consists in fixing the amount of HF exchange a priori, was behind the development of the PBE0 functional. This functional form was obtained by supplying the PBE functional with a predefined amount of HF exchange. The PBE0 functional has shown very good performance for structural, thermodynamic,
kinetic and spectroscopic – magnetic, infrared and electronic – properties. The way in which the functional is derived and the lack of empirical parameters fitted to specific properties, make the PBE0 model a widely applicable method for both quantum chemistry and condensed matter physics. It has been reported improved performance of the PBE0 functional over the B3LYP for properties of systems containing light and heavy metals.\textsuperscript{62,63}

One of the newest classes of functionals are the hybrid-meta-GGA. This type of functionals combine the inclusion of HF exchange with the meta GGA approach. The M06 functional belongs to this class, and has revealed improved performance over some meta and hybrid functionals.\textsuperscript{64} This functional, besides of the Laplacian dependency of the density, includes a dependence on the electronic kinetic-energy density ($\tau$). This is up-spin down-spin dependent. This functional was also parameterized to be self-interaction error (SIE) free. The SIE results from the fact that the interaction of an electron with itself is accounted for in the exchange-correlation functionals obtained from the LDA, GGA and MGGA approaches. The hybrid functionals partly correct the SIE due to the inclusion of HF exchange.\textsuperscript{65} The SIE results from a physically unreasonable property that leads to poor performance of the functionals especially in describing systems with non-integer number of electrons.\textsuperscript{66} This means that the functionals which are not free from SIE have problems also in describing transition states of chemical reactions (especially those involving homolytic bond cleavage) and charge-transfer complexes. For solids and surfaces, it has been recently show that hybrid DFT functionals that contain a certain amount of HF exchange are necessary to accurately describe the electronic states of nonmetallic solids and the defects in metal oxides.\textsuperscript{67-71} In order to properly describe the electronic properties of the defects of TiO$_2$ surfaces for example, it is necessary to recur to the usage of functionals that incorporate a certain amount of HF exchange.\textsuperscript{70} The pure DFT functionals, due to the SIE, fail to give a localized character to trapped electron states and holes in TiO$_2$ surface defects. When unpaired electronic states are present in the system, this type of functionals will tend do delocalize the electron density in order to minimize the SIE, thus giving results for electron density in surface defects that are poor when compared with experimental data. This situation has been evident whenever pure DFT functionals were used for describing defects in large band gap semiconductors and insulators.\textsuperscript{72} Other discrepancies were found in the type of minima for the bonding between HO$^*$ and H$_2$O when these systems were described with pure DFT functionals.\textsuperscript{73,74} These situations can be improved by using HF exchange in the functionals. The empirical formalisms to correct for the SIE did not lead to good performing functionals
for systems where fractional charge behavior is present, polarizabilities of polymers and dissociation of molecules.\textsuperscript{75}

Efficient basis sets based have been developed based on the usage of an effective core potential (ECP) which replaces the true electron core potential.\textsuperscript{76} The number of electrons treated explicitly is then much smaller and the number of required electronic states and basis set size is reduced significantly. This approach made possible the computational study of metals for which the explicit treatment of their core electrons makes such calculations computationally prohibitive. Relativistic effects can also be incorporated in ECP basis sets.\textsuperscript{77} This is particularly useful for calculations involving heavier transition metals or lanthanide and actinide elements.\textsuperscript{78}

### 2.5 Conceptual density functional theory

The frontier molecular orbital based approaches to describe the reactivity of organic compounds are an effective way to relate intrinsic properties of organic compounds with their reactivity.\textsuperscript{79-81} Simple descriptors such as electronegativity, electron affinities, ionization potentials, hardness and softness have been used for predicting trends on the reactivity of many molecules. These approaches are classified as global reactivity descriptors (GRD). They became wide-spread in recent times because electronic structure calculations are easier to perform due to the increase in computational power. The above mentioned GRD arise naturally from DFT as they can be described in terms of the electron density as follows

\[
\mu = \left( \frac{\partial E}{\partial N} \right)_Z = -\chi \tag{9}
\]

\[
\mu = \begin{cases} 
-\text{IP} \ (Z - 1 < N < Z) \\
-\text{EA} \ (Z < N < Z + 1) 
\end{cases} \tag{10}
\]

From Equation (9) it can be seen that the chemical potential ($\mu$) is dependent on the derivative of the energy ($E$) with respect to the number of electrons ($N$). The second equality in this equation corresponds to the electronegativity ($\chi$) and is valid for $N = Z$. $Z$ is the nuclear charge of the atom, IP is the ionization potential of the system and EA is the electron affinity. The chemical potential $\mu$ of DFT measures the escaping tendency of the electrons from the system. The slope, $(dE/dN)_Z$, of Equation (9) is equal to the chemical potential $\mu$ of DFT.\textsuperscript{82} Equation (10) was used by Perdew and coworkers to derive

\[
\varepsilon_{\text{max}} = \begin{cases} 
-\text{IP} \ (Z - 1 < N < Z) \\
-\text{EA} \ (Z < N < Z + 1) 
\end{cases} \tag{11}
\]

where $\varepsilon_{\text{max}}$ is the maximum Kohn-Sham (KS) occupied orbital energy. The interpretation of Equation (11) is that the highest occupied KS orbital energy of an $N$-electron system is the negative of the ionization potential within
Because of the discontinuity on \( \mu \) in Equation (9), it can be inferred from Equation (10) that \( \mu = -IP \) for all the \( Z-1 < N < Z \) and \( \mu = -EA \) for all \( Z < N < Z+1 \). When \( N = Z \), \( \mu \) becomes the average value \( \mu = -(IP+EA)/2 \) which is related to the Mulliken definition of electronegativity \( (\chi) \). According to Mulliken’s definition, \( \chi = (IP+EA)/2 \). In an analogous way, from Equation (11), when \( Z-1 < N < Z \), \( \varepsilon_{\text{max}} \) represents the energy of one KS orbital corresponding to the highest occupied molecular orbital (HOMO), whereas when \( Z < N < Z+1 \), \( \varepsilon_{\text{max}} \) represents the KS energy of the orbital corresponding to the lowest unoccupied molecular orbital (LUMO) of the \( Z \) electron system or the HOMO of the \( Z+1 \) electron system.

From the formulation of Parr and Pearson was developed the concept of chemical hardness \( (\eta) \). This is the second derivative of \( E \) with respect to \( N \) according to

\[
\eta = \left( \frac{\partial^2 E}{\partial N^2} \right)_Z = \left( \frac{\partial \mu}{\partial N} \right)_Z
\]

This definition can be expressed in terms of the KS orbitals as the gap between the HOMO-LUMO energies. Within Hartree-Fock theory, the interpretation of the orbitals energies is done according to

\[
I_i = E_{\text{HF}}(N-1,i) - E_{\text{HF}}(N)
\]

where \( I_i \) is the ionization potential of an electron in an orbital \( \phi_i \). \( E_{\text{HF}}(N) \) is the energy of the \( N \)-electron system before ionization and \( E_{\text{HF}}(N-1,i) \) is the energy of the system after removal of the electron from \( \phi_i \). From Koopmans theorem arises the assumption that the removal of an electron from \( \phi_i \) will generate a stable conformation with respect to further variation in \( \phi_i \). This approach neglects the fact that the removal of an electron produces a rearrangement on the spatial charge distribution in the remaining orbitals which leads to the stabilization of the ion. In a similar way as with the HF approach, with DFT, the application of the frontier molecular orbital approach is valid within the region of validity of the Koopmans theorem. Politzer et al. have shown that the hybrid DFT functionals in spite of producing a systematic deviation from the experimental ionization potentials, produce the same deviation for all of the valence orbitals. The deviations obtained for different molecular systems were larger than those obtained for the same molecule, but still smaller than 58 kJ·mol⁻¹.

### 2.6 Surface chemistry and catalysis from density functional theory

DFT is a very important tool for the study of surface chemistry. The challenge of understanding surface processes at the microscale level is very often only overcome with the aid of theoretical methods. Given the large size of the systems usually necessary to describe a surface, the wave function based methods are not possible to apply due to their computational...
demands. DFT is then the computational tool of choice for surface chemists. There has been a rich history of success of DFT in the design of new catalysts—e.g. ammonia synthesis—i.e. in the understanding of the several surface reaction steps that usually characterize solid-liquid and solid-gas reactions, and in the design of better materials from the prediction of their surface chemistry.

Interactions between molecules and surfaces can be described theoretically using several methods. From these, the most commonly applied method for investigating adsorption and reactivity is the use of density functional theory (DFT) and periodic boundary conditions (PBC). Another approach is to use a finite cluster model of the surface. Both approaches have their advantages and disadvantages. While PBC provides a physically sound treatment of the periodicity of extended surfaces, surface defects can be a hard task to model with PBC due to the interactions of artificial periodicity of the defects introduced. Even though this can be overcome by using very large unit cells, it increases the computational time and cost significantly. Besides of the restricted offer of codes using the PBC approach which permit the access to wave function methods and consequently also to hybrid Hartree-Fock/DFT, the usage of hybrid functionals with PBC requires computational power which is prohibitively expensive for many users. In general, the major source of error when using the PBC approach is due to limitations of the electronic structure methods used, i.e. pure DFT.

The cluster approach has the advantage that one can make use of the vast array of quantum chemical methods that have been developed and implemented. Quantum chemical methods such as hybrid density functionals, double hybrid density functionals or higher-order wave function methods are readily available tools for modeling surfaces using cluster models. The cluster approach is best suited for describing local phenomena such as interactions on catalytically active sites. Due to its low computational cost, the cluster approach is efficient for modeling the reactivity of surface defects, which can be crucial for understanding experimentally observed kinetics. On the other hand, finite size effects can be detrimental for obtaining reliable data for properties of extended surfaces. Such problems can be overcome by increasing the cluster size or by using the embedded cluster model approach. For the modeling of adsorption on ideal/perfect surfaces, the cluster approach becomes inefficient due to the size of the cluster required to accurately represent the system. Nevertheless, in real applications of engineered or natural materials, ideal surfaces are rarely present. Instead, solid surfaces are typically polycrystalline and display a defective surface-structure.

Effects of cluster size and edge geometry on calculated adsorption energies, were recently investigated in a work where cluster models were used in
combination with hybrid and double hybrid exchange-correlation
functionals.\textsuperscript{94} Accurate adsorption energies onto mineral surfaces were
obtained with two layers thickness clusters that retained the correct
stoichiometry and charge of the surfaces. The authors calculated adsorption
energies as a function of cluster size and concluded that beyond size-
convergence, the maximum error introduced was 16 kJ·mol\textsuperscript{-1} for adsorption
from gas phase. Convergence was achieved with clusters only large enough
to include the surface atoms and groups involved in the binding of the
adsorbate.

The information obtained from the application of DFT methods to surfaces
has led to a deeper understanding of surface processes. For example the
determination of the BEP parameter described in Equation (8) has proved a
very useful tool for leading the design of catalysts or for the understanding
of surface reactivity. This concept had its boom due to the availability of DFT
calculations at a larger scale.\textsuperscript{47} A deeper understanding of surface reactivity
has been possible due to the application of DFT. For example, a topic that has
been debated for many decades is the role of defects in surface reactivity.\textsuperscript{100}
Recently, using adsorption experiments and DFT calculations it has been
shown that the N\textsubscript{2} dissociation on the Ru(0001) surface is totally dominated
by steps.\textsuperscript{101} The adsorption rate at the steps is over 9 orders of magnitude
higher than on the terraces. The corresponding calculated difference in
activation energy is 145 kJ·mol\textsuperscript{-1}. The lower barrier at the step sites is
attributed to a combination of electronic and geometrical effects. In another
study, it was reported that the presence of surface defects in MgO films
lower the activation energies for reactions with water by as much as 60%.\textsuperscript{102}
The same reaction that has considerable activation energy on an ideal
surface, can occur without energy barrier at surface defects. Consequently,
for non-ideal surfaces, the overall reaction rate is often determined by
interactions with defective sites.\textsuperscript{96} The physical-chemical properties of
surface defects and the chemical reactivity of such sites are mainly the
results of local structural and electronic properties, and less dependent on
the properties of the extended surface.\textsuperscript{42} The properties of surface defects are
above all dependent on the types of atom exposed at the defects, their
oxidation states, their coordination/ligand field and their Lewis acidity.
There are several examples in the literature showing that defective surface
sites, displaying coordinatively unsaturated metal atoms, can enhance the
reactivity of a material.\textsuperscript{102-104} In general, the interactions between adsorbates
and surfaces are a localized event. It has been suggested that a local
approximation for the study of surface reactivity could be applied without
loss of precision. This because the resultant structures from adsorbed
molecules onto metal atoms that constitute surfaces often resemble the
structures of the corresponding organometallic complexes.\textsuperscript{105} In the case of a
defective surface, the degree of localization of these interactions is even higher. As such, the approaches such as the $d$-band type model, breaks when applied to defects, as the density of states of the bulk is broken at the surface and even more extensively at defect sites. The more undercoordinated an atom is at a defect, the more “free-atom-like-character” the density of states of that atom will have. At the bulk, the density of states is influenced by the bonding on the extended crystal structure and the extent of delocalization of the bulk atoms electrons is significant. In the defects, the lack of extended structure adds more localized character to the orbitals of atoms at those sites. This makes the orbitals of the defect atom more available for interactions with adsorbates than the orbitals of less undercoordinated surface atoms. At these sites the adsorption is generally more exothermic.

The effect of the defects on reaction mechanisms can be categorized as electronic or geometric. A linear BEP relation between adsorption energies and reaction activation energy barriers is only obtained when the contribution to the overall relation comes either from the electronic or geometric component. Otherwise, the BEP plot deviates from an ideal straight line. This is actually the case for real surfaces (i.e. not grown in UHV controlled conditions) where the BEP relations are very seldom linear due to the coexistence of electronic and geometric contributions to the surface reaction pathways.

2.7 Methodology for the combined experimental-theoretical study of surface reactions.

In the present thesis a combined experimental-theoretical methodology for the study of the catalytic decomposition of $\text{H}_2\text{O}_2$ on the surface of transition metal and lanthanide oxides under “real” conditions is used. The reaction systems are composed of particle suspensions of the oxides in aqueous solutions. These systems have complex dynamics due to the presence of surface defects, surface hydroxylation and solvation. Also, the pH of the media has an effect on the surface charge which can disturb the adsorption of charged adsorbates. The experimental study of such systems is challenging. Nevertheless, the determination and analysis of experimental kinetic and mechanistic data from these real systems combined with a theoretical investigation of the processes involved in the reaction mechanisms can aid the understanding of the microscale phenomena that leads to a certain macroscale observation.
3 Experimental and computational details

3.1 Experimental details

3.1.1 Instrumentation

Specific surface areas of the powders were determined using the B.E.T. method of isothermal adsorption and desorption of a gaseous mixture consisting of 30% N₂, 70% He in a Micrometrics Flowsorb II 2300 instrument. γ-Irradiation was performed using a MDS Nordion 1000 Elite Cs-137 γ-source with a dose rate of 0.15 Gy·s⁻¹, this value was determined using Fricke dosimetry. X-ray powder diffractograms (XRD) were obtained at 293 K, using CuKα radiation, on a PANalytical X´pert instrument. Powders were mounted into the sample holders rings. The data was collected over the range 3° ≤ 2θ ≤ 80°, with a step size of 0.033° (2θ). Data evaluation was done using The High Score Plus software package and the PDF-2 database was used for matching the experimentally obtained diffractograms. The samples were weighted to ±10⁻⁵ g, in a Mettler Toledo AT261 Delta Range microbalance. The reactions were performed under inert atmosphere with a constant flux of N₂ gas (AGA Gas AB) and at constant known temperatures using a Huber CC1 or a Lauda E100 thermostat, calibrated against a Therma 1 Thermometer coupled to a submersible K-type (NiCrNi) temperature probe, with a precision of ± 0.1 K. UV/Vis spectra were collected using a WPA Lightwave S2000 or a WPA Biowave II UV/Vis Spectrophotometer. Trace elemental analysis were performed using the technique of inductively coupled plasma spectroscopy, on a Thermo Scientific iCAP 6000 series ICP spectrometer. The analysis for Zr was performed at the wavelength of 343.823 nm and that of U at 367 and 385.9 nm.

3.1.2 Materials

All the solutions used in this study were prepared using water from a Millipore Milli-Q system. ZrO₂ (CAS[1314-23-4], Aldrich 99%); TiO₂ (CAS[13463-67-7], Alfa Aesar, 99.9%); Y₂O₃ (CAS[1314-36-9], Alfa Aesar, 99.9%); Fe₂O₃, (CAS[1309-37-1], Aldrich 99%); CeO₂, (CAS[1306-38-3], Alfa Aesar 99.99% ); HfO₂, (CAS[12055-23-1], Alfa Aesar 99.95%); Gd₂O₃, (CAS[12064-62-9], Aldrich 99.9%); and CuO, (CAS[1317-38-0], Aldrich 99.99%) were used without further purification. To the XRD data was applied a Rietveld refinement using ICSD-26488 as a starting model and yielded the following cell parameters for ZrO₂: a) 5.1458(2) Å, b) 5.2083(3) Å, c) 5.3124(3) Å. These values are in good agreement with the cell parameters attributed to the monoclinic phase. For TiO₂ the Rietveld refinement yielded a composition 88.5% anatase and 11.5% rutile. The obtained cell parameters for TiO₂ are: a = b) 3.7856(2) Å, c) 9.5058(5) Å for the anatase phase and a = b) 4.5914(8) Å, c) 2.9539(10) Å for the rutile phase. The obtained cell
parameters for Y\textsubscript{2}O\textsubscript{3} are: \(a\) 10.60398(9) Å, attributed to the cubic (bixbyite-type) structure.\textsuperscript{111} These crystal structures match the information provided by the materials manufacturers. Based on this, the measurement of the crystal structures for the other oxides was not done and the crystal structures considered are those provided by the oxides manufacturers.

Uranium dioxide pellets and powder provided by Westinghouse Atom AB and SIMFUEL pellets provided by Atomic Energy of Canada Limited were used in the experiments after being washed with a solution 10 mM NaHCO\textsubscript{3} (Merck, p.a.) for 14 hours. The total impurities present on the UO\textsubscript{2} powder correspond to 48 μg/g U. The weight of the pellets was determined to be 5.3 g for the Westinghouse pellet and 7.9 g for the SIMFUEL pellet. The composition of the SIMFUEL pellet expressed as weight ratios to uranium is as follows: Sr(2.74 × 10\textsuperscript{-3}), Y(6.46 × 10\textsuperscript{-4}), Zr(5.72 × 10\textsuperscript{-3}), Mo(5.24 × 10\textsuperscript{-3}), Ru(3.80 × 10\textsuperscript{-3}), Rh(6.25 × 10\textsuperscript{-3}), Pd(2.93 × 10\textsuperscript{-3}), Ba(3.68 × 10\textsuperscript{-3}), La(8.77 × 10\textsuperscript{-3}), Ce(8.77 × 10\textsuperscript{-3}), Nd(1.00 × 10\textsuperscript{-2}).

The specific surface area of the powders are the average of three measurements, each consisting of a sorption and a desorption isotherm whose values were also averaged. The B.E.T. specific surface areas of the oxides are: ZrO\textsubscript{2} (5.0 ± 0.2 m\textsuperscript{2}·g\textsuperscript{-1}); TiO\textsubscript{2} (38.9 ± 0.2 m\textsuperscript{2}·g\textsuperscript{-1}); Y\textsubscript{2}O\textsubscript{3} (4.48 ± 0.03 m\textsuperscript{2}·g\textsuperscript{-1}); Fe\textsubscript{2}O\textsubscript{3} (9.0 ± 1.0 m\textsuperscript{2}·g\textsuperscript{-1}); CeO\textsubscript{2} (14.3 ± 1.0 m\textsuperscript{2}·g\textsuperscript{-1}); HfO\textsubscript{2} (10.0 ± 0.1 m\textsuperscript{2}·g\textsuperscript{-1}); Gd\textsubscript{2}O\textsubscript{3} (1.7 ± 0.1 m\textsuperscript{2}·g\textsuperscript{-1}); CuO (15.3 ± 0.1 m\textsuperscript{2}·g\textsuperscript{-1}); UO\textsubscript{2} powder (5.4 ± 0.2 m\textsuperscript{2}·g\textsuperscript{-1}). The surface area of the uranium pellets was calculated by using a geometrical approach and produced the values of 352 mm\textsuperscript{2} for the UO\textsubscript{2} pellet and 471 mm\textsuperscript{2} for the SIMFUEL pellet.

The particle sizes were supplied by the manufactures. For Gd\textsubscript{2}O\textsubscript{3} the value was obtained using the technique of confocal profilometry: The particle sizes are as follows: ZrO\textsubscript{2} (< 5 μm); TiO\textsubscript{2} (32 nm); Y\textsubscript{2}O\textsubscript{3} (< 10 μm); Fe\textsubscript{2}O\textsubscript{3} (< 5 μm); CeO\textsubscript{2} (14. μm); HfO\textsubscript{2} (44. μm); Gd\textsubscript{2}O\textsubscript{3} (15 nm); CuO (< 50 nm); UO\textsubscript{2} (16 μm).

### 3.1.3 Kinetic experiments

The H\textsubscript{2}O\textsubscript{2} solutions were prepared from a 30% standard solution (Merck). The particle suspensions where the reactions with H\textsubscript{2}O\textsubscript{2} took place consisted of ZrO\textsubscript{2} [0.5–4.5 g]; TiO\textsubscript{2} [0.146–0.341 g]; Y\textsubscript{2}O\textsubscript{3} [1.269–2.961 g]; Fe\textsubscript{2}O\textsubscript{3} [0.2–1.5] g; CeO\textsubscript{2} [0.06–0.52] g; HfO\textsubscript{2} [0.75–0.1] g; Gd\textsubscript{2}O\textsubscript{3} [0.25–1.0] g; CuO [0.0025–0.1] g in 50 mL of H\textsubscript{2}O\textsubscript{2} 0.5 mM. For the test experiments concentrations of H\textsubscript{2}O\textsubscript{2} that varied in the range [0.2–6.0] mM were used. The H\textsubscript{2}O\textsubscript{2} solutions were prepared from a 30% standard solution (Merck). After extraction of the sample from the reaction vessel, the sample was filtered through a Gema Medical 0.45μm–25mm Cellulose Acetate syringe filter. Subsequently, a sample volume of 0.2 mL was used for the measurement of the H\textsubscript{2}O\textsubscript{2} concentration. The concentration of H\textsubscript{2}O\textsubscript{2} was determined using the Ghormley triiodide method. In this method, I\textsuperscript{-} is oxidized to I\textsuperscript{3-} by H\textsubscript{2}O\textsubscript{2}.\textsuperscript{112,113}
The absorbance of the product I$_3$ is measured spectrophotometrically at the wavelength of 350 nm. Initially, a calibration curve where the absorbance of I$_3$ was plotted as a function of the concentration of H$_2$O$_2$ was obtained in the range 0.02 to 0.8 mM resulting in a linear correlation between absorbance and concentration.

### 3.1.4 Mechanistic study

The mechanistic study involved scavenging HO radicals formed during decomposition of H$_2$O$_2$. This was done by means of the reaction between tris(hydroxymethyl)aminomethane, (Tris) (CAS[77-86-1]), BDH Chemicals, 99%) or N-[Tris(hydroxymethyl)methyl]-3-aminopropanesulfonic acid sodium salt; (TAPS-Na$^+$) (CAS[91000-53-2], Sigma > 99%) and the HO radicals to produce formaldehyde. The formaldehyde produced was then quantified spectrophotometrically at 368 nm, by using a modified version of the Hantzsch reaction. In this method the formaldehyde reacted with acetoacetanilide AAA (CAS[102-01-2], Alfa Aesar > 98%) in the presence of ammonium acetate (CAS[631-61-8], Lancaster 98%) to form a dihydropyridine derivative which has the maximum absorption wavelength at 368 nm. A calibration curve plotting the absorbance of the dihydropyridine derivative as a function of formaldehyde concentration was obtained at 368 nm, giving a linear correlation between absorbance and concentration, in the concentration range 0.15 $\mu$M to 1 mM in formaldehyde. The plotting of the calibration curve for formaldehyde required the preparation of several solutions of CH$_2$O with different rigorously known concentrations in the concentration range mentioned above. It was then necessary to proceed to the accurate determination of the concentration of formaldehyde in the solution used initially (CAS[50-00-0]), Aldrich 37% wt in H$_2$O) using the iodometric method. The solutions and respective standardizations necessary to follow the iodometric method procedure were prepared as stated in the cited paper and as described elsewhere. The error associated with the determination of the concentration of formaldehyde in the initial solution was 1.15%.

The reaction media for HO• detection during decomposition of H$_2$O$_2$ consisted of: ZrO$_2$ (1.5 g) or TiO$_2$ (0.197 g) or Y$_2$O$_3$ (1.678 g) or Fe$_2$O$_3$ (1.5 g) or CeO$_2$ (1.6 g) or HfO$_2$ (2.25 g) or Gd$_2$O$_3$ (3.0 g) or CuO (0.06 g) with H$_2$O$_2$ (5 mM) and Tris (20mM) in 50 ml at a pH of 7.5.

### 3.1.5 Affinity of ZrO$_2$, TiO$_2$ and Y$_2$O$_3$ for the HO radical

The study of the scavenging capacities of the oxides towards HO• consisted of $\gamma$-irradiating samples of the oxides in the presence of Tris. The reaction media used was ZrO$_2$ (1.5 g) or TiO$_2$ (0.197 g) or Y$_2$O$_3$ (1.678 g) in 50 ml Tris (20 mM) solution at pH 7.5. The pH was adjusted with HCl. The detection of
the amount of HO radicals scavenged by Tris followed the same procedure as described above for the mechanistic study.

3.1.6 Determination of H\textsubscript{2} and O\textsubscript{2} during H\textsubscript{2}O\textsubscript{2} decomposition

All the solutions were purged with ultra-high purity argon (99.9999\%). Hydrogen and oxygen were determined in deaerated samples using an inline technique employing a gas chromatograph. Ultrahigh purity argon was used as the carrier gas with a flow rate of about 50 mL/min. The argon passed through a constant flow regulator, an injection septum, a four-way valve and into a 5 m molecular sieve column of an SRI 8610C gas chromatograph with a thermal conductivity detector. The samples cells were connected to the gas analysis system, purged of air, isolated, crushed and then the gases injected into the carrier gas stream. H\textsubscript{2} and O\textsubscript{2} were determined in each of the samples. Calibration of the detector was performed by injecting pure H\textsubscript{2} and O\textsubscript{2} with a gastight microliter syringe. The error in gas measurement was estimated to be about 5%.

3.1.7 Measurement of adsorption equilibrium constants for adsorption of Tris and TAPS onto ZrO\textsubscript{2}

The determination of the amount of Tris and TAPS in solution was done following a basic competition kinetic scheme. According to reference\textsuperscript{116} the bleaching of methylene blue solutions (1-16 μM) under γ-radiolysis increases linearly up to doses on the order of 500 Gy. Here, a linear correlation for the bleaching of a methylene blue solution (18 μM) was observed as a function of γ dose up to 90 Gy, which was the dose used for measurement of the competition kinetic experiments. The methylene blue concentration was measured with UV-Vis spectrophotometry at 664 nm. γ-irradiation of a methylene blue solution undergoes less bleaching in the presence of another HO• radical scavenger than does a pure methylene blue solution. This protection is due to competition for the HO• radical between the methylene blue and the added HO• radical scavenger\textsuperscript{117}. The competition kinetics between Tris or TAPS and the methylene blue for the HO• radical was used to determine the amount of Tris or TAPS removed from solution by adsorption. The reduction in bleaching of a methylene blue (18 μM) solution and the increase in concentration of Tris or TAPS is linear in the concentration range of 50-250 μM of Tris or TAPS. The measurement of the adsorption parameters for Tris and TAPS was done at 298 K using solutions of varying concentration of adsorbate. After adsorption equilibrium was reached, a sample aliquot was taken and filtered and the competition kinetic analysis with methylene blue was performed. The reaction media for the adsorption study consisted of 5 ml of Tris or TAPS solution with concentrations in the range 100-500 μM and ZrO\textsubscript{2} (2.5 g, Surface Area = 8.4 m\textsuperscript{2}) at pH 7.5 adjusted with HCl. The lower value of concentration of Tris
3 Experimental and computational details

and TAPS for which was possible to determine adsorption parameters using competition with methylene blue was 50 μM.

3.1.8 Effects of HO• scavengers on the products of H₂O₂ decomposition

The effects of the HO• scavengers on the products of H₂O₂ decomposition were investigated using reaction media consisting of 2 ml of H₂O₂ (10 mM) solution and ZrO₂ (0.4 g, Sa = 1.34 m²) or TiO₂ (0.149g, Sa = 1.42 m²) or CuO (0.631g, Sa = 1.34) at pH 7.5. The pH was adjusted with HCl. Varying concentrations of Tris and TAPS in the range [0–200] mM were used.

3.2 Computational details

DFT calculations were performed using the molecular cluster model approach and the software package Jaguar 7.7.(Ref.119). Cluster geometries were optimized at the B3LYP/LACVP*+ level of theory. The basis set LACVP*+ is a combination of the split valence basis set 6-31+G(d) and the Los Alamos effective core potential for transition metals. Single-point evaluations of energies were performed using exchange-correlation functionals built on the generalized gradient approximation (GGA), namely the pure density functionals PBE(54,60,61) and PWPW91(120); the pure meta functional M06-L(121), the hybrid functionals PBE0(60,61), B3LYP, and B3LYP* (122); and the hybrid meta functional M06(123). The M06 functional has shown improved accuracy for describing transition metal chemistry and medium range attractive dispersion interactions.124 In addition, the effects of adding an empirical attractive dispersion term (−f(R)C₆·R⁻⁶) to the B3LYP functional according to the method of Grimme, were investigated.125 The functionals used are further described in Table 1 in terms of the amount of Hartree-Fock exchange (EHF) incorporated and whether or not the electronic kinetic energy density (τ) depends on the spin.

Table 1. Density functionals used in this work described in terms of: the percentage of Hartree-Fock exchange (EHF); up-spin and down-spin electronic kinetic energy density (τ).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP</th>
<th>B3LYP*</th>
<th>M06</th>
<th>M06-L</th>
<th>PBE0</th>
<th>PBE</th>
<th>PWPW91</th>
</tr>
</thead>
<tbody>
<tr>
<td>ExHF(%)</td>
<td>20</td>
<td>15</td>
<td>27</td>
<td>0</td>
<td>25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>τ</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

Single point calculations were performed with the split valence triple-ζ basis set LACV3P**, which is supplemented with polarization and diffuse functions on all atoms. The following convergence criteria were used for all geometry calculations (atomic units): rms gradient < 3 × 10⁻⁴; maximum gradient < 4.5 × 10⁻⁴; rms step < 1.2 × 10⁻³; maximum step < 1.8 × 10⁻³; maximum change in total energy between two consecutive steps < 5 × 10⁻⁵.
The cluster models implemented conform to the three principles proposed to model metal oxides using clusters. These principles are: the neutrality principle, the stoichiometry principle and the coordination principle.

The adsorption energies reported herein were calculated as

$$\Delta E_{\text{ads}} = E_{\text{adsorbate/cluster}} - (E_{\text{adsorbate}} + E_{\text{cluster}})$$

where $E_{\text{adsorbate/cluster}}$, $E_{\text{adsorbate}}$, $E_{\text{cluster}}$, represent the electronic energies in gas-phase for the adsorbate binding to the cluster, free adsorbate and bare cluster respectively. This means that the more negative the adsorption energy, the stronger is the adsorption.

Transition states were located using the quadratic synchronous transit (QST) method implemented in Jaguar 7.7. Corrections to obtain zero-point vibrational effects and the thermodynamic potential enthalpy ($H$) were calculated from a Hessian matrix of harmonic force constants using the partition functions of an ideal -/non-interacting gas at $T = 298.15$ K and $P = 1$ atm. The vibrational frequencies obtained from the Hessian matrix were also used to verify the first-order saddle point nature of the transition states.

### 3.2.1 Conceptual DFT

The functional PBE0 has shown improved performance over other hybrid functionals in describing lanthanide and heavy metal chemistry. For the clusters of HfO$_2$, CeO$_2$ and Gd$_2$O$_3$ the geometries were optimized using the PBE0 functional and the CSDZ++ basis set for the metal atoms and 6-31G++ for H and O. CSDZ is the implementation in Jaguar of the Cundari and Stevens ECP basis set for lanthanides. For the clusters of transition metals the LACVP++ basis set was used for geometry optimizations. Single-point evaluations of the energies were performed using PBE0 with LACV3P++ basis set for the clusters of transition metals. For HfO$_2$, CeO$_2$ and Gd$_2$O$_3$ were used the CSDZ++ basis set for the metal atoms and the 6-311G++ for the O and H atoms. For the non-lanthanides, the Mulliken electronegativities of the cations present in the metal oxides were determined from the IP and EA both calculated at the PBE0/LACV3P++ using fully analytical accuracy and the maximum grid density.

### 4. Results and discussion

#### 4.1 Kinetics and activation energies for H$_2$O$_2$ decomposition on transition metal oxide surfaces

The reactions of H$_2$O$_2$ with particle suspensions of ZrO$_2$, Y$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, HfO$_2$, CeO$_2$, Gd$_2$O$_3$, CuO and UO$_2$ were investigated. H$_2$O$_2$ can react with metal oxides via different pathways.
One-electron oxidation:

\[ \text{H}_2\text{O}_2 \, (\text{aq}) + M^x \, (s) \rightarrow M^{x+1} \, (s) + \text{HO}^-(\text{ads})/(\text{aq}) + \text{HO}^* \, (\text{ads})/(\text{aq}) \]  (R9)

Two-electron oxidation:

\[ \text{H}_2\text{O}_2 \, (\text{aq}) + M^x \, (s) \rightarrow M^{x+2} \, (s) + 2\text{HO}^- \, (\text{ads})/(\text{aq}) \]  (R10)

Catalytic decomposition:

\[ \text{H}_2\text{O}_2 \, (\text{aq}) + M^y \, (s) \rightarrow 2\text{HO}^* \, (\text{ads})/(\text{aq}) + M^y \, (s) \]  (R11)

\[ \text{HO}^* \, (\text{ads})/(\text{aq}) + \text{H}_2\text{O}_2 \, (\text{ads})/(\text{aq}) \rightarrow \text{HO}_2^* \, (\text{ads})/(\text{aq}) + \text{H}_2\text{O} \, (\text{ads})/(\text{aq}) \]  (R12)

\[ 2\text{HO}_2^* \, (\text{ads})/(\text{aq}) \rightarrow \text{H}_2\text{O}_2 \, (\text{aq}) + \text{O}_2 \, (\text{g}) \]  (R13)

for which the overall known stoichiometry for processes (R11) to (R13) is

\[ \text{H}_2\text{O}_2 \, (\text{aq}) \rightarrow \text{H}_2\text{O} \, (\text{l}) + \text{1/2O}_2 \, (\text{g}) \]  (R14)

where \( M \) represents a metal cation in a metal oxide, in the oxidation state \( x \) or \( y \). In all the above mentioned metal oxides with the exception of \( \text{UO}_2 \), the metal cation is in its maximum oxidation state and cannot be further oxidized. At the surface of such materials, the reaction of \( \text{H}_2\text{O}_2 \) occurs via catalytic decomposition. It has been suggested that the reduction of \( \text{Ti}^{4+} \) in \( \text{TiO}_2 \) by \( \text{H}_2\text{O}_2 \) can take place.\(^\text{130}\) Though, due to the lack of detailed experimental evidence and discussion of this reaction, it is considered as a side process that in case it occurs at all, is expected to have a very small yield when compared with the main path for the reactivity of \( \text{H}_2\text{O}_2 \) – the catalytic decomposition. Nevertheless, in this work, the possibility that this reaction occurs when \( \text{H}_2\text{O}_2 \) reacts with \( \text{ZrO}_2 \) was investigated. With \( \text{UO}_2 \), \( \text{H}_2\text{O}_2 \) can react both via a redox mechanism and by catalytic decomposition.\(^\text{131}\) In general, the catalytic decomposition of \( \text{H}_2\text{O}_2 \) on a solid surface is a spontaneous process at temperatures that range from room temperature up to 286 °C and its reported activation energy ranges from 21 kJ·mol\(^{-1}\) to 96 kJ·mol\(^{-1}\), depending on the type of surface and on factors such as the oxidation state of the metal.\(^\text{132}\) Reaction (R13) corresponds to the chain termination and occurs via the disproportionation of two hydroperoxyl radicals as represented. When reaction (R13) occurs with pure water as a solvent, its activation energy is 25 kJ·mol\(^{-1}\), in the temperature range [274-316] K.\(^\text{133}\)
4.1.1 ZrO$_2$

The evaluation of the kinetics and energetics of the catalytic decomposition of H$_2$O$_2$ has to be done within a temperature and pH range where the spontaneous non-catalyzed decomposition of H$_2$O$_2$ is negligible when compared to the rate of its decomposition on the surface of the oxide itself. In neutral water, from the species involved in the reactions (R11) to (R13), only dissociation of HO$_2^\cdot$ needs to be considered, since the pK$_a$'s for H$_2$O$_2$, HO$^\cdot$, and HO$_2^\cdot$ are 11.8, 11.9 and 4.88 respectively. The HO$_2^\cdot$ (hydroperoxyl radical) is a weak acid and is also the protonated form of the superoxide radical anion which can be formed at and bind to the surface of ZrO$_2$ according to the following reaction

\[
\text{HO}_2^\cdot \text{(ads)/(aq)} \xrightarrow{\text{ZrO}_2} \text{H}^+ \text{(aq)} + \text{O}_2^\cdot \text{(ads)}
\]  

the superoxide anion radical can be stabilized by adsorption onto the surface of the ZrO$_2$ and has been used previously as a spin probe for the study of surfaces. This radical binds to the surface by coordination with exposed Zr$^{4+}$ surface cations.

The decomposition of H$_2$O$_2$ on the surface of ZrO$_2$ was investigated at $T = 298.15$ K by studying the variation in the concentration of H$_2$O$_2$ as a function of reaction time. The obtained data is represented in Figure 5 which shows the normalized concentration of H$_2$O$_2$ ($[\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0$) as a function of reaction time. $[\text{H}_2\text{O}_2]_t$ is the concentration of H$_2$O$_2$ at the time $t$ and $[\text{H}_2\text{O}_2]_0$, is the concentration of H$_2$O$_2$ at $t = 0$.

![Figure 5](image.png)

Figure 5. Normalized concentration of H$_2$O$_2$ ($[\text{H}_2\text{O}_2]_0 = 0.5$ mM) as a function of reaction time in the reaction with ZrO$_2$ (1.5 g; $S_\text{a} = 7.5$ m$^2$) at $T = 298.15$ K in 50 ml H$_2$O. © American Chemical Society.

A plot of ln($[\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0$) using the data of Figure 6, shows good agreement with a first-order kinetic law. Nevertheless, the order of the reaction with respect to H$_2$O$_2$ was confirmed by application of the method of
Results and discussion

The initial reaction rates were determined for different concentrations of H$_2$O$_2$ and for the same amount of ZrO$_2$. A plot of ln(initial reaction rate) as a function of ln([H$_2$O$_2$]) was obtained at $T = 313.15$ K. The reaction media consisted of ZrO$_2$ (1.5 g; $Sa = 7.5$ m$^2$) and different concentrations of H$_2$O$_2$ that ranged from 0.5 to 6 mM. Application of a linear regression of the data yielded a slope of $0.98 \pm 0.04$. Considering the experimental error associated with this value it is possible to conclude that the reaction is first-order with respect to H$_2$O$_2$. The kinetic data for decomposition of H$_2$O$_2$ on ZrO$_2$ was then treated as a first-order process. The first-order rate constant obtained from the linear correlation shown in Figure 6, for the temperature $T = 298.15$ K is $k_1 = (6.15 \pm 0.04) \times 10^{-5}$ s$^{-1}$.

![Figure 6](image_url)  

**Figure 6.** ln([H$_2$O$_2$]$_t$/[H$_2$O$_2$]$_0$) as a function of reaction time (s) for the decomposition of H$_2$O$_2$ on ZrO$_2$ using the data shown in Figure 5. © American Chemical Society.

The second order rate constant ($k_2$) was determined according to Equation (3). The $Sa/V$ dependence of the first-order rate constant is shown in Figure 7.

![Figure 7](image_url)  

**Figure 7.** $k_1$ for decomposition of H$_2$O$_2$ (0.5 mM) as a function of ZrO$_2$ $Sa/V$ obtained at $T = 298.15$ K. © American Chemical Society.
The value of $k_2$ obtained from the slope of the plot of Figure 7 for the reaction at $T = 298.15$ K is $k_2 = (2.39 \pm 0.09) \times 10^{-10}$ m·s$^{-1}$. As expected, this value is very far from the value corresponding to a diffusion controlled reaction for which the rate constant is in the order of $10^{-5}$ m·s$^{-1}$ for particles of this size.$^9$

For the determination of the Arrhenius activation energy, the rate constants were obtained as a function of the reaction temperature for the temperature interval $T = [294.15-353.15]$ K with a temperature step of 5 K.

![Figure 8](image-url) Arrhenius plot of $\ln(k)$ as a function of $1/T$ (K) for $T = [294.15-353.15]$ K with a temperature step of 5 K. © American Chemical Society.

The values of $\ln(k_1)$ as a function of the inverse of the temperature are represented in Figure 8. For the determination of $E_a$, for each temperature value, three rate constant values were obtained in three different experiments and the resulting values were averaged. The temperature dependence of the reaction rate constant displays Arrhenius behavior. The rate constant varied from $(5.670 \pm 0.003) \times 10^{-5}$ s$^{-1}$ to $(4.50 \pm 0.01) \times 10^{-4}$ s$^{-1}$, for $T = 298.15$ and $T = 353.15$ K respectively. The half-life varied from 198.0 min for the reaction at 298.15 K, to 26.3 min for the reaction at 353.15 K. The obtained $E_a$ value for decomposition of H$_2$O$_2$ on the ZrO$_2$ particle suspension in the temperature range $T = [298.15-353.15]$ K is $33 \pm 1$ kJ·mol$^{-1}$. This value is in good agreement with previously published data for similar systems.$^{132}$ The corresponding enthalpy of activation obtained from the Eyring plot is $\Delta H^\ddagger = 30 \pm 1$ kJ·mol$^{-1}$. When comparing these values with the bond dissociation energy (BDE) of the O-O bond in H$_2$O$_2$,$^{136}$ which is $\approx 208$ kJ·mol$^{-1}$, or the BDE for cleavage of the H-OOH bond in H$_2$O$_2$ which is $\approx 372$ kJ·mol$^{-1}$,$^{137}$ it is evident that the oxide-liquid interface is acting as a catalyst and lowers substantially the energy barrier necessary to eventually cleave one of these bonds. Judging from these BDE values, most likely, the main reaction path will be through the cleavage of the HO-OH bond.

To verify if the reaction of H$_2$O$_2$ with ZrO$_2$ is purely catalytic decomposition, involving no extensive modifications of the surface of the
catalyst, a B.E.T. measurement of the surface area of the powder was performed. This was done on three types of ZrO$_2$ samples: prior to immersion in the aqueous reactant solution, after immersion in water during a time interval equal to the reaction time, and after reaction with hydrogen peroxide. Prior to the B.E.T. specific surface area determination, the solid was dried in vacuum at $T = 353.15$ K and $P = 0.1$ Pa, the data obtained are summarized in Table 2.

**Table 2.** Specific surface areas of the fresh powder determined by the B.E.T. method, after immersion in water at $T = 353$ K and after reaction with H$_2$O$_2$ at $T = 353$ K.

<table>
<thead>
<tr>
<th>ZrO$_2$ Sample</th>
<th>specific surface area (m$^2$·g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh powder</td>
<td>5.0 ± 0.2</td>
</tr>
<tr>
<td>after immersion in water at $T=353$ K</td>
<td>5.0 ± 0.2</td>
</tr>
<tr>
<td>after reaction with H$_2$O$_2$ in aqueous media at $T=353$ K</td>
<td>5.0 ± 0.3</td>
</tr>
</tbody>
</table>

As can be seen (Table 2), no detectable changes occurred on the specific surface area of the solid due to immersion in water or due to the reaction with H$_2$O$_2$. To evaluate possible changes in the crystal structure of ZrO$_2$, a comparison of the XRD diffractograms obtained before and after reaction was done. Prior to the collection of the XRD data, the reaction between ZrO$_2$ and H$_2$O$_2$ was performed until complete consumption of H$_2$O$_2$. The obtained cell parameters $a = 5.1497(7)$ Å, $b = 5.2123(7)$ Å, $c = 5.3164(8)$ Å, are in excellent agreement with the values obtained before the reaction took place (see experimental details section). This means that no extensive change occurred in the crystal structure of the powder during the course of the reaction.

The superoxide anion radical formed according to Reaction (R15) is an active reductive species and can for example reduce transition metal cations present in oxides such as Fe$^{3+}$ in Fe$_2$O$_3$. Translated to the case of Zr(IV) this reaction would be

$$\text{O}_2^{-\bullet} (\text{ads}) + \text{Zr}^{4+} (\text{s}) \rightarrow \text{O}_2 (\text{g}) + \text{Zr}^{3+} (\text{s})/(\text{aq}) \quad (\text{R16})$$

the possible reduction of Zr(IV) following a process similar to Reaction (R16) was investigated. If occurring, this reaction would cause a deviation from the equilibrium stoichiometry of the surface of the oxide, in aqueous solution this would lead to the subsequent release of Zr into the solution. This was investigated first by measuring traces of Zr in solution using inductively coupled plasma spectroscopy (I.C.P.). The I.C.P. technique allows for the detection of the total amount of an element with no distinction for oxidation state. A blank measurement was previously performed on a sample taken from a ZrO$_2$ (1.5 g) particle suspension in 50 ml of water where ZrO$_2$ was
exposed for a period of time equal to the reaction time with H$_2$O$_2$. Subsequently the solid particles were filtered and the measurement of the blank was done. The measurement to track the possible release of zirconium due to reaction with H$_2$O$_2$ was made after the reaction reached completion. The I.C.P. measurement was performed after filtration of the solid particles from the reactant solution. The value for the increase in concentration of Zr in solution after reaction is $(9.1 \pm 0.2) \times 10^{-8}$ M. When comparing the amount of zirconium in solution and the amount of hydrogen peroxide present that had reacted (i.e. 5 orders of magnitude higher), it can be seen that the increase in the amount of zirconium in solution is negligible. Under these conditions, Reaction (R16) if it occurs is a side reaction that has a small contribution to the overall H$_2$O$_2$ reactivity in this system. If Reaction (R16) would occur extensively – causing a change in the oxidation state of Zr(IV) to other state besides Zr(0) – it could have repercussions on the crystal structure of the solid. Eventually creating defects in the lattice due to the replacement of Zr(IV) by Zr atoms in different oxidation states and consequent re-arrangement of the surface to compensate for the non-equilibrium stoichiometry of the new created lattice. If this process occurs extensively, it would lead to different cell parameters before and after reaction. This is not observed and significant reduction of Zr (IV) by superoxide anion radical is not detectable in this system.

A behavior very close to zeroth-order kinetics can be obtained when the amount of H$_2$O$_2$ is in large excess when compared to the number of adsorption sites available on the oxide surface. In this way it is possible to fit the data to zeroth-order kinetics minimizing the error of such approximation. For a reaction which is zeroth-order with respect to H$_2$O$_2$, the reaction rate constant will be independent of the concentration of H$_2$O$_2$. The lower limit of ZrO$_2$ mass, where the reaction changes from first-order to zeroth-order is $\approx 0.5$ g; $S_a = 2.5$ m$^2$. For masses of ZrO$_2$ smaller than 0.5 g in 50 ml H$_2$O$_2$ (0.5 mM) solution, the reaction starts to obey a zeroth-order kinetic law. The zeroth-order rate constant obtained at $T = 298.15$ K with ZrO$_2$ (0.224 g) in 50 ml H$_2$O$_2$ (0.5 mM) solution, is $k_0 = (2.0 \pm 0.1) \times 10^{-5}$ M·s$^{-1}$. Obviously, with the reduction in ZrO$_2$ mass, the transition from first-order to zeroth-order is not sudden. There is a range of ZrO$_2$ masses where the reaction follows a non-integer rate law whose coefficient lays somewhere between 0 and 1.

As described in section 2.3, the pH of the aqueous media is an important parameter in surface processes in solution and can affect the rate of uptake of an adsorbate by a surface. In the case of a system where hydrogen-bonded structures between adsorbate and solute and/or surface are possible, the pH effect might become even more important. H$_2$O$_2$ is capable of forming stable cyclic hydrogen-bonded structures in solution. Also, for the system H$_2$O$_2$-ZrO$_2$, changes in the pH of the reactant solution can alter the concentration
of superoxide radical trapped on the surface by affecting the attractive/repulsive forces between the superoxide radical and the surface. In order to evaluate the effect of pH changes on the rate of decomposition of H₂O₂, the \( k_0 \) values were determined for different pH values. The pH was adjusted with Tris/HCl buffer. The data obtained are represented in Figure 9.

![Figure 9](image)

**Figure 9.** \( k_0 \) as a function of solution pH obtained at 298.15 K for decomposition of H₂O₂ (0.5 mM) on ZrO₂ (0.5 g) particle suspensions in 50 ml solution. © American Chemical Society.

The pH of the point of zero charge of ZrO₂ is \( \approx 6.5 \). As can be seen (Figure 9), the zeroth-order rate constant is linearly dependent on the pH of the solution. When considering the zeroth-order rate constant – where the surface concentration of H₂O₂ is close to constant with the course of the reaction – it is possible to have a picture of what is the effect of the amount of surface superoxide radical in the reaction rate. Since within the range of studied pH values the deprotonation of H₂O₂ and HO• radical are not to be considered due to their higher \( pK_a \) values, the effect pH on the eventual intermediate reaction species translates in the amount of superoxide radical present at the surface. Reaction (R11) is dependent on the number of available sites on the surface where H₂O₂ can bind to. As such, the amount of O₂•⁻ bound to the surface should have an impact on the overall reaction rate by causing alterations in the interactions between H₂O₂ and the active sites in the surface due to the occupancy of the latter by the superoxide anion radical. This means that the rate at which H₂O₂ reaches the catalytically active surface sites will be decreased causing the reaction rate constant to decrease. Following this reasoning, as expected, when considering the amount of superoxide radical present on the surface, the \( k_0 \) is higher the less superoxide is present on the surface. On the other hand, it is also necessary to consider the possible effect of the presence of the buffer system used to adjust the pH.
4.1.2 Other transition metals and lanthanide oxides

4.1.2.1 TiO$_2$ and Y$_2$O$_3$

Data for H$_2$O$_2$ decomposition on a series of oxide materials has revealed that the rate constants can differ substantially depending on the type of oxide.$^{129}$ In order to better understand the processes involved in the decomposition of H$_2$O$_2$ it is important to understand how its kinetics and energy barriers differs for different materials. This information can possibly be correlated with properties of the materials which will be reflected by the kinetic parameters and which can help understand the mechanisms involved.

The reactions of H$_2$O$_2$ with TiO$_2$ and Y$_2$O$_3$ were investigated using the same $SA/V$ of oxides as for ZrO$_2$. This allows for direct comparison of kinetic parameters and reveals possible differences on the catalytic efficiency of the oxides. The data obtained for the reaction of H$_2$O$_2$ with TiO$_2$ and Y$_2$O$_3$ are represented in Figure 10.

![Figure 10](image)

Figure 10. Normalized concentration of H$_2$O$_2$ as a function of reaction time in the reaction with TiO$_2$ (♦) and Y$_2$O$_3$ (●) at T = 298.15 K with [H$_2$O$_2$]$_0$ = 0.5 mM. © American Chemical Society.

Besides the data shown here previously for ZrO$_2$, it has been reported that for similar systems the catalytic decomposition of H$_2$O$_2$ follows first-order kinetics.$^{142-144}$ However, as shown for ZrO$_2$, the apparent reaction order is strongly dependent on the $(SA/V)$. When the available surface area of catalyst is in excess, first-order kinetics are observed. Zeroth-order kinetics are observed when the available surface area is too small. It can be seen (Figure 10) that the reaction of H$_2$O$_2$ with TiO$_2$ and Y$_2$O$_3$ deviates from first-order kinetics and two different trends can be observed. In both cases, after a fast initial consumption of H$_2$O$_2$, the reaction is slowed down significantly. To extract the rate constants, the two visible trends for each reaction in Figure 10 were considered to be the result of two different processes governing the kinetics. The nature of the two different kinetic trends of this reaction were investigated by performing the reaction in the presence of Tris buffer and tracking the formation of intermediate HO$^*$ radical with reaction time (this will be discussed in the section 4.2.2 of this thesis). The highlighted areas in
Figure 10 denote the regions where the kinetics start to be controlled by the decomposition of H$_2$O$_2$ after the initial adsorption process. By extracting the rate constants from these plots, taking into account the fact that the two processes, adsorption and decomposition of H$_2$O$_2$ occur on different time scales, it is possible to obtain the kinetics of decomposition and adsorption of H$_2$O$_2$ with minimal errors associated. The $k_0$ values obtained at $T = 298.15$ K, are $k_0 = (5.9 \pm 0.6) \times 10^{-6}$ M·s$^{-1}$ for the decomposition of H$_2$O$_2$ on TiO$_2$ and $k_0 = (4.5 \pm 0.4) \times 10^{-5}$ M·s$^{-1}$ for the decomposition of H$_2$O$_2$ on Y$_2$O$_3$. The rate constants for adsorption under the same experimental conditions were extracted from the initial parts of the plots. The obtained $k_1$ values for this process are $k_1 = 3 \times 10^{-3}$ s$^{-1}$ for adsorption of H$_2$O$_2$ on TiO$_2$ and $k_1 = 6 \times 10^{-3}$ s$^{-1}$ for adsorption of H$_2$O$_2$ on Y$_2$O$_3$. The good separability of processes allowing the extraction of coherent kinetic data for either the adsorption or decomposition means that it is possible to obtain a $k_2$ value for the adsorption process and in a similar way, to extract a quantity from the region of the plot that shows zeroth-order kinetics and which correlates with the catalytic capacity of the surfaces. The data used for determination of the $k_2$ values for adsorption are represented in Figure 11.

![Figure 11](image-url)

**Figure 11.** First order rate constants for adsorption of H$_2$O$_2$ (0.5 mM) in 50 ml, as a function of solid-surface-area-to-solution-volume-ratio ($S_a/V$), for adsorption onto Y$_2$O$_3$ and TiO$_2$ at $T = 298.15$ K. © American Chemical Society.

The $k_2$ values for adsorption of H$_2$O$_2$ extracted from these plots are $k_2 = (5.2 \pm 0.6) \times 10^{-8}$ m·s$^{-1}$ for adsorption onto TiO$_2$ and $k_2 = (1.5 \pm 0.2) \times 10^{-7}$ m·s$^{-1}$ for adsorption onto Y$_2$O$_3$. As for the $k_2$ value obtained for reaction with ZrO$_2$, these values are far from the diffusion limit. However, the $k_2$ values for adsorption onto TiO$_2$ and Y$_2$O$_3$ are 2 and 3 orders of magnitude higher than the $k_2$ value obtained for decomposition of H$_2$O$_2$ onto ZrO$_2$ respectively.

A plot of the variation of the $k_0$ values for decomposition of H$_2$O$_2$ as a function of $S_a/V$ gives the rate constant $k_c$ which represents the catalytic
capacity of the surface. The obtained data for the variation of $k_0$ with mass of oxide is shown in Figure 12.

Figure 12. Zeroth-order rate constants as a function of solid-surface-area-to-solution-volume-ratio ($Sa/V$) for the reactions of decomposition of H$_2$O$_2$ with Y$_2$O$_3$ (■) and TiO$_2$ (●) at $T = 298.15$ K. © American Chemical Society.

The rate constants $k_c$ extracted from the plots of Figure 12, obtained at $T = 298.15$ K are $k_c = (1.93 \pm 0.02) \times 10^{-13} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ for reaction with TiO$_2$ and $k_c = (2.08 \pm 0.06) \times 10^{-11} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ for reaction with Y$_2$O$_3$. These values describe the catalytic efficiency of the surfaces, per unit of surface area. It can be seen that the catalytic efficiency of the surface of Y$_2$O$_3$ in catalyzing the decomposition of the H$_2$O$_2$, is higher than that of TiO$_2$ by 2 orders of magnitude.

Determining the amount of H$_2$O$_2$ removed from solution – in the initial process of adsorption onto the surfaces – as a function of oxide surface area, allows determination of the number of adsorption sites capable to accommodate H$_2$O$_2$, per unit surface area. The resulting data obtained for this study is represented in Figure 13.
Figure 13. Variation in the amount \((n)\) of \(\text{H}_2\text{O}_2\) molecules removed from solution by adsorption onto \(\text{TiO}_2\) (♦) and \(\text{Y}_2\text{O}_3\) (■) as a function of the surface area of solid \((S_a)\) present in the reaction system at \(T = 298.15\) K. Initial \([\text{H}_2\text{O}_2]\) = 0.5 mM; \(V = 50\) mL. © American Chemical Society.

The number of surface (or interfacial) sites capable of adsorbing \(\text{H}_2\text{O}_2\) is \((2.0 \pm 0.1) \times 10^{-4} \text{ mol·m}^{-2}\) for \(\text{TiO}_2\) and \((1.00 \pm 0.02) \times 10^{-4} \text{ mol·m}^{-2}\) for \(\text{Y}_2\text{O}_3\). It is important to note that these numbers are for the adsorption of \(\text{H}_2\text{O}_2\) onto the hydroxylated surfaces in equilibrium, in a \(\text{H}_2\text{O}\) solution. These numbers might vary with the course of the reaction due to the adsorption of \(\text{H}_2\text{O}_2\) reaction products onto the surfaces. These products can eventually adsorb onto the same surface sites preferred for \(\text{H}_2\text{O}_2\) adsorption. The accumulation of reaction products at those sites could ultimately hinder the adsorption of \(\text{H}_2\text{O}_2\). This issue will be discussed more in depth later in this work.

To determine the Arrhenius activation energies and the activation enthalpies for the reactions of decomposition of \(\text{H}_2\text{O}_2\) on \(\text{TiO}_2\) and \(\text{Y}_2\text{O}_3\) the \(k_0\) values were studied as a function of temperature in the temperature intervals \(T = [298.15–348.15]\) K for \(\text{TiO}_2\) and \(T = [293.15–308.15]\) K for \(\text{Y}_2\text{O}_3\). The respective Arrhenius plots are represented in Figure 14.
The resulting $E_a$ values for decomposition of H$_2$O$_2$ on TiO$_2$ and Y$_2$O$_3$ are $37 \pm 1$ kJ·mol$^{-1}$ and $47 \pm 5$ kJ·mol$^{-1}$ respectively. The pre-exponential factors are $18 \pm 2$ M·s$^{-1}$ for TiO$_2$ and $6228 \pm 6$ M·s$^{-1}$ for Y$_2$O$_3$. The $\Delta H^\ddagger$ values for H$_2$O$_2$ decomposition are $34 \pm 1$ kJ·mol$^{-1}$ for TiO$_2$ and $44 \pm 5$ kJ·mol$^{-1}$ for Y$_2$O$_3$.

Similarly, the activation energies of adsorption ($E_{a,ads}$) were calculated from plots of the logarithm of the $k_1$ values for adsorption as a function of the inverse of the temperature. The activation enthalpies of adsorption ($\Delta H_{ads}^\ddagger$) were determined using the same $k_1$ values. The $k_1$ values for adsorption were extracted from the initial parts of the plots of ln([H$_2$O$_2$]$_t$/[H$_2$O$_2$]$_0$) as a function of reaction time (Figure 10). The resulting data are: $E_{a,ads} = 23 \pm 1$ kJ·mol$^{-1}$ for adsorption of H$_2$O$_2$ on TiO$_2$ and $E_{a,ads} = 32 \pm 3$ kJ·mol$^{-1}$ for adsorption of H$_2$O$_2$ on Y$_2$O$_3$. The frequency factors are $A = 21 \pm 2$ s$^{-1}$ for the adsorption on TiO$_2$ and $A = 2625 \pm 3$ s$^{-1}$ for the adsorption on Y$_2$O$_3$. The obtained $\Delta H_{ads}^\ddagger$ are: $21 \pm 2$ kJ·mol$^{-1}$ for adsorption of H$_2$O$_2$ onto TiO$_2$ and $\Delta H_{ads}^\ddagger = 29 \pm 3$ kJ·mol$^{-1}$ for adsorption of H$_2$O$_2$ onto Y$_2$O$_3$. The obtained values for $A$ differ by 2 orders of magnitude – the higher value is for adsorption onto Y$_2$O$_3$. The frequency factors for a first-order process represent the number of events (controlling the kinetics) per unit time. When applied to adsorption, they are related with the accessibility of an adsorbate in reaching the adsorption sites which are able to accommodate the adsorbate. The difference in the values of $A$ for adsorption onto TiO$_2$ and Y$_2$O$_3$ mean that Y$_2$O$_3$ is a more efficient adsorbent for H$_2$O$_2$. The values obtained for the adsorption site density at the surfaces of the oxides reveal that even though the surface of TiO$_2$ has twice as much adsorption sites – capable of accommodating H$_2$O$_2$ – per unit surface area than Y$_2$O$_3$, the Y$_2$O$_3$ surface sites are more easily accessible for H$_2$O$_2$. 

Figure 14. Arrhenius plots using the $k_0$ values for the reaction of decomposition of H$_2$O$_2$ on TiO$_2$ (■) and Y$_2$O$_3$ (♦). © American Chemical Society.
4 Results and discussion

4.1.2.2 $\text{Fe}_2\text{O}_3$, $\text{CuO}$, $\text{HfO}_2$, $\text{CeO}_2$ and $\text{Gd}_2\text{O}_3$

The reactions of $\text{H}_2\text{O}_2$ with powder suspensions of: $\text{CeO}_2$, $\text{Fe}_2\text{O}_3$, $\text{HfO}_2$, $\text{Gd}_2\text{O}_3$ and $\text{CuO}$ in aqueous media were also investigated. The goal is to have a complete set of data for $\text{H}_2\text{O}_2$ reactivity with different materials. This is important data for modeling kinetics or thermodynamics of processes that involve these chemicals, but, it is also used later in this work in conjunction with DFT calculations to describe these reaction systems in terms of intrinsic properties of the materials.

From the kinetic experiments it was verified that $\text{Fe}_2\text{O}_3$, $\text{CuO}$ and $\text{Gd}_2\text{O}_3$ display higher overall reactivity towards $\text{H}_2\text{O}_2$. This caused the half-lifes of the reactions to become too short to allow collection of a fair quantity of reliable kinetic data. For this reason it was necessary to use a smaller total surface area of these oxides than for all the other oxides studied in this work. The variation in concentration of $\text{H}_2\text{O}_2$ with reaction time, for the reactions of $\text{H}_2\text{O}_2$ with $\text{CeO}_2$, $\text{HfO}_2$, $\text{CuO}$, $\text{Gd}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ at $T = 298.15 \text{ K}$ are shown in Figure 15.

![Figure 15](image_url)

Figure 15. Normalized concentration of $\text{H}_2\text{O}_2$ (initially 0.5mM in 50 ml) as a function of reaction time for the reaction with $\text{CeO}_2$ (■), $\text{CuO}$ (♦), $\text{HfO}_2$ (▲), $\text{Gd}_2\text{O}_3$ (●) and $\text{Fe}_2\text{O}_3$ (▬) at $T = 298.15 \text{ K}$. $\text{Sa}$: $\text{Fe}_2\text{O}_3$ (4.5 m²), $\text{CeO}_2$ (7.5 m²); $\text{CuO}$ (0.3 m²); $\text{HfO}_2$ (7.5 m²); $\text{Gd}_2\text{O}_3$ (1.7 m²).

It can be seen (Figure 15) that in the reaction with $\text{H}_2\text{O}_2$, the only oxide that deviates in terms of kinetic behavior is $\text{Gd}_2\text{O}_3$. Interestingly, when using the same surface area as for the other oxides, $\text{Gd}_2\text{O}_3$ displayed a high overall reactivity towards $\text{H}_2\text{O}_2$. When using a surface area of 1.7 m², the reactivity of $\text{Gd}_2\text{O}_3$ towards $\text{H}_2\text{O}_2$ is considerably lower than for the other oxides. The initial adsorption of $\text{H}_2\text{O}_2$ on $\text{Gd}_2\text{O}_3$ is a fast process when compared with the decomposition of adsorbed $\text{H}_2\text{O}_2$. By reducing the surface area, the capacity to adsorb $\text{H}_2\text{O}_2$ is reduced and the catalytic decomposition becomes the predominant process responsible for the disappearance of $\text{H}_2\text{O}_2$ from
Results and discussion

solution. This was also observed for the reaction with ZrO$_2$, when masses of oxide lower than 0.5 g ($S_a = 2.5 \text{ m}^2$) were used. In order to have comparable energetic data, the process determining the kinetics, from which the data is extracted, has to be the same for all oxides. It can be seen that for all oxides there is an initial faster disappearance of H$_2$O$_2$ from solution which is followed by a process that obeys first-order kinetics. Under the conditions of the experiments (i.e. for these values of $S_a$ of oxide and [H$_2$O$_2$]$_0$), the time frame for the adsorption process is different for the various oxides but considering the total reaction time, its contribution to the overall reaction is relatively small. The treatment of kinetic data for the calculation of the $E_a$ and $\Delta H^\ddagger$ values used the kinetic data obtained from the first-order process that follows the initial adsorption. The $k_1$ values obtained from the data of Figure 15 are given in Table 3. In Figure 15 it is evident that while for CuO and HfO$_2$, the plot shapes resemble first-order behavior during most of the reaction time, for CeO$_2$ and Gd$_2$O$_3$ the reaction fits a first-order kinetic treatment only within a limited H$_2$O$_2$ concentration range. This differs from the cases of ZrO$_2$, TiO$_2$ and Y$_2$O$_3$. For ZrO$_2$ the first-order kinetic behavior was observed during the whole reaction time, while for TiO$_2$ and Y$_2$O$_3$ the reaction kinetics are zeroth-order after the fast initial adsorption step that obeys first-order. For these two oxides it was then possible to extract the adsorption kinetic and energetic data due to the good separability of the adsorption from the subsequent process. This is not the case for the other oxides.

The mass dependency of the $k_1$ values for the reactions with Fe$_2$O$_3$, CuO, CeO$_2$, HfO$_2$ and Gd$_2$O$_3$ are shown in Figure 16.

![Figure 16](image)

**Figure 16.** Variation in first-order rate constant with the surface-area-to-solution-volume-ratio ($S_a/V$) of oxide for decomposition of H$_2$O$_2$ (0.5 mM; 50 ml) at $T = 298.15 \text{ K}$. Fe$_2$O$_3$ ( ■ ), CuO (♦), CeO$_2$ (■), HfO$_2$ (▲) and Gd$_2$O$_3$ (●).

It can be seen that for the reaction with HfO$_2$ the value of $k_1$ shows a high mass dependency, while in the opposite extreme lays CeO$_2$. The
corresponding obtained $k_2$ values and the value of the intercept at zero coordinate ($b_2$) are given in Table 3.

Table 3. Obtained $k_1$, $k_2$ and $b_2$ for decomposition of H$_2$O$_2$ (0.5 mM; 50 mL) catalyzed by different oxides at $T = 298.15$ K. $k_1$ were obtained with the following $S_a$ of oxides: ZrO$_2$ (7.5 m$^2$), TiO$_2$ (7.5 m$^2$), Y$_2$O$_3$ (7.5 m$^2$), Fe$_2$O$_3$ (4.5 m$^2$), CeO$_2$ (7.5 m$^2$); CuO (0.3 m$^2$); HfO$_2$ (7.5 m$^2$); Gd$_2$O$_3$ (1.7 m$^2$). Note: The rate constant values for TiO$_2$ and Y$_2$O$_3$ are $k_0$ (M·s$^{-1}$) and the $k_c$ and $b_c$ values are obtained from $k_0$ values.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>$k_2$ (m·s$^{-1}$)</th>
<th>$b_2$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>(6.15 ± 0.04) × 10$^{-5}$</td>
<td>(2.39 ± 0.09) × 10$^{-10}$</td>
<td>3 × 10$^{-5}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>(2.1 ± 0.4) × 10$^{-4}$</td>
<td>(3.0 ± 0.06) × 10$^{-9}$</td>
<td>2 × 10$^{-4}$</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>(1.7 ± 0.5) × 10$^{-4}$</td>
<td>(2.80 ± 0.07) × 10$^{-8}$</td>
<td>5 × 10$^{-6}$</td>
</tr>
<tr>
<td>CuO</td>
<td>(1.90 ± 0.05) × 10$^{-4}$</td>
<td>(1.23 ± 0.06) × 10$^{-9}$</td>
<td>6 × 10$^{-6}$</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>(4.3 ± 0.9) × 10$^{-4}$</td>
<td>(2.78 ± 0.02) × 10$^{-9}$</td>
<td>1 × 10$^{-5}$</td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>(3.6± 0.3) × 10$^{-5}$</td>
<td>(9.4 ± 1) × 10$^{-10}$</td>
<td>6 × 10$^{-6}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>$k_0$ (M·s$^{-1}$)</th>
<th>$k_c$ (mol·m$^{-2}$·s$^{-1}$)</th>
<th>$b_c$ (M·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>(5.9± 0.6) × 10$^{-6}$</td>
<td>(1.93± 0.02) × 10$^{-13}$</td>
<td>(1.55± 0.05) × 10$^{-9}$</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>(4.5± 0.4) × 10$^{-5}$</td>
<td>(2.08± 0.06) × 10$^{-12}$</td>
<td>(2.3± 0.1) × 10$^{-5}$</td>
</tr>
</tbody>
</table>

The fastest heterogeneous process (Table 3) is for the reaction with CeO$_2$ while the slowest is for the case of ZrO$_2$. The decomposition of H$_2$O$_2$ catalyzed by Gd$_2$O$_3$ is the slowest from all the materials showing first-order kinetics for decomposition and the fastest is that on the surface of Fe$_2$O$_3$. The higher value of $b_2$ for the case of Fe$_2$O$_3$ indicates that the apparent reactivity of H$_2$O$_2$ has a higher contribution from a homogeneous process than in the case of the other materials. Most likely the homogenous process is the Fenton reaction which takes place in the bulk solution due to the presence of dissolved Fe$^{2+}$ released from the surface of Fe$_2$O$_3$. Fe$^{2+}$ can be formed by reduction of Fe$^{3+}$ initiated by a product of H$_2$O$_2$ decomposition, the HO$_2$ radical and which involves directly O$_2$• to form O$_2$, following a scheme similar to what is represented in Reaction (R16).

The $E_a$ values were obtained from plots of the logarithm of the first-order rate constants as a function of the inverse absolute temperature. The temperature dependence of the reaction rate constants for the different oxides was studied in the temperature interval $T = [298.15–334.15]$ K for Fe$_2$O$_3$, CuO, HfO$_2$ and $T = [298.15–353.15]$ K for CeO$_2$ and Gd$_2$O$_3$. The upper temperature limit is the value below which it was possible to collect enough data points for the H$_2$O$_2$ concentration as a function of time, with minimal errors associated. This because the reaction becomes too fast to allow proper data collection above a certain temperature. The upper limit of error
considered acceptable was 5%. The Arrhenius plots are represented in Figure 17 and the resulting data are shown in Table 4.

Figure 17. Arrhenius plots for the first-order rate constant as a function of reaction temperature for the decomposition of H$_2$O$_2$ (0.5mM; 50 mL) catalyzed by different oxides. CeO$_2$ (■), CuO (♦), HfO$_2$ (▲), Gd$_2$O$_3$ (●) and Fe$_2$O$_3$ (▬). *Sa:* Fe$_2$O$_3$ (4.5 m$^2$), CeO$_2$ (7.5 m$^2$); CuO (0.3 m$^2$); HfO$_2$ (7.5 m$^2$); Gd$_2$O$_3$ (1.7 m$^2$).

Table 4. Arrhenius activation energies ($E_a$), surface area normalized pre-exponential factors ($A$), and enthalpies of activation ($\Delta H^\ddagger$) for the catalytic decomposition of H$_2$O$_2$ on different oxides. *Reaction parameters obtained from first-order kinetics except where stated otherwise.*

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_a$ (kJ·mol$^{-1}$)</th>
<th>$\Delta H^\ddagger$ (kJ·mol$^{-1}$)</th>
<th>$A$ (s$^{-1}$)</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>33 ± 1</td>
<td>30 ± 1</td>
<td>30</td>
<td>&lt; 5 μm</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>37 ± 1</td>
<td>34 ± 1</td>
<td>18 M·s$^{-1}$</td>
<td>32 nm</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>44 ± 5</td>
<td>44 ± 5</td>
<td>6.2 × 10$^3$ M·s$^{-1}$</td>
<td>&lt; 10 μm</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>51 ± 1</td>
<td>44 ± 1</td>
<td>1.8 × 10$^3$</td>
<td>&lt; 5 μm</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>40 ± 1</td>
<td>37 ± 1</td>
<td>1.4 × 10$^3$</td>
<td>14 μm</td>
</tr>
<tr>
<td>CuO</td>
<td>76 ± 1</td>
<td>73 ± 1</td>
<td>8.6 × 10$^{10}$</td>
<td>&lt; 50 nm</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>60 ± 1</td>
<td>57 ± 1</td>
<td>1.1 × 10$^7$</td>
<td>44 μm</td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>63 ± 1</td>
<td>60 ± 1</td>
<td>1.5 × 10$^7$</td>
<td>15 nm</td>
</tr>
</tbody>
</table>

The obtained $E_a$ and $\Delta H^\ddagger$ values vary significantly for the different oxides studied (Table 4). This indicates that the activation energies are most likely dictated by microstructural properties of the particles such as the type of atoms present at the catalytically active surface sites and the extent of hydroxylation at these sites. In aqueous solution, most of the metal oxide surfaces are hydroxylated, due to dissociative adsorption of H$_2$O.$^{146}$ The structure and extent of this hydroxylation layer will in turn determine the rigidity of the interfacial water layers which lay slightly further from the surface but still interact with the surface HO-groups. The more rigid the
interfacial layers of adsorbed water, the higher the barrier for diffusion of H$_2$O$_2$ through the layer before it reaches the catalytically active surface sites. Hence, the affinity of the surfaces towards water is expected to contribute to the observed activation energy barriers for H$_2$O$_2$ decomposition. Also the intermediate products formed during decomposition of H$_2$O$_2$ are oxygen species that in spite of being radicals, to some extent, have “water-like” properties such as the ability to form hydrogen bonds.

4.2 Mechanistic studies – the HO radical as primary product of H$_2$O$_2$ decomposition

The kinetic and energetic data presented in section 4.1.2 shows that for the catalytic decomposition of H$_2$O$_2$ on different metal oxide surfaces the energy barriers and the pre-exponential factors differ widely. This is an indicator that distinct interfacial/surface processes might be involved or have different importance in the reactions with the different materials.

Reactions (R11) to (R13) have been suggested based on liquid phase data for H$_2$O$_2$ reactivity. Direct evidence for the formation of HO radicals as primary product and their further role in the decomposition of H$_2$O$_2$ at a solid-liquid interface are processes which are not completely understood. It has been suggested that even at an interface with a surface, these radicals can react further with H$_2$O$_2$ to form HO$_2^*$ and O$_2^{-}$. In previous studies of this type of reaction, EPR/ESR measurements revealed the presence of HO$_2^*$, O$_2^{-}$, and peroxyl radical species on the surface of different oxides. These radicals are normally short-lived and reactive but due to their stabilization by forming bonds with the surfaces, they had become long-lived. It was also demonstrated that the possible existence of such chemical species is a factor that depends on the solution pH.

In order to better understand the formation of intermediate HO$^*$ during the decomposition of H$_2$O$_2$, a mechanistic study was performed. According to the proposed mechanism, the HO$^*$ is formed in the decomposition of H$_2$O$_2$ in the presence of a metal oxide according to Reaction (R11). Studies on the dynamics of formation of HO$^*$ produced during decomposition of H$_2$O$_2$ can help understand the process of formation of HO$^*$ during the reaction. These studies involved determining the rate of formation of HO$^*$ and compare its dynamics with the rate of consumption of H$_2$O$_2$. The chemical yield for the formation of formaldehyde upon reaction of the HO$^*$ with Tris was determined by quantifying the amount of formaldehyde produced from a known amount of HO$^*$ in the system. For that, a calibration curve was obtained by performing an experiment where a known amount of HO$^*$ was produced by $\gamma$-radiolysis and scavenged by Tris producing formaldehyde according to the scheme shown in Figure 18.
4 Results and discussion

Figure 18. Reaction of tris(hydroxymethyl)aminomethane (Tris) with HO· producing formaldehyde and a radical species which can further react to form a more stable species.

The method for the spectrophotometric detection of CH$_2$O, based on the Hantzsch reaction,$^{151}$ has been used in previous works. In this case however it was necessary to use a modified version of this method.$^{152}$ The use of acetoacetanilide (AAA) instead of acetylacetone or 2,4-pentadione avoids interferences with H$_2$O$_2$ which made this technique possible to apply with good sensitivity to the systems studied here. A scheme of the reactions involved is shown in Figure 19.

Figure 19. Formation of a pyridyl derivative from the reaction of CH$_2$O with acetoacetanilide (AAA) in the presence of ammonium acetate.

For the calibration of the method the principle based in Reactions (R2) and (R3) occurring upon radiolysis of water was used. The amount of hydroxyl radicals produced during water radiolysis was quantified according to Equation (2). The set of data obtained for the amount of CH$_2$O produced as a function of the amount of hydroxyl radicals present in solution upon irradiation of a solution 20 mM in tris/HCl buffer, pH = 7.5 in 50 ml H$_2$O at $T$ = 293.25 K, are represented in Figure 20.
Figure 20. Comparison between the rate of formation of hydroxyl radicals (■) in water radiolysis and the corresponding concentration of formaldehyde (♦) obtained using the modified Hantzsch method. © American Chemical Society.

The yield of the method, when comparing the concentration of CH₂O produced, with the accumulated concentration of hydroxyl radicals present in solution is 35%. This means that 35% of the HO• present in the system react with Tris buffer to produce CH₂O. A result well below 100% would be expected since according to scheme 2, the reaction of HO• with Tris can take place in other positions of the molecule besides the α-hydrogen atom of the alcohol group that results in the formation of CH₂O. Hence, the reaction can follow different pathways producing different compounds not detectable by the modified Hantzsch method. The detection limit obtained for CH₂O is 0.5 μM which in the homogeneous system corresponds to a concentration in HO• equal to 1.43 μM. This is the limit of detection of the method obtained by using solutions of different formaldehyde concentration, which were put in contact with ZrO₂ particle suspensions. A literature value obtained for a system where no solid was present is 0.1 μM in CH₂O. It can be concluded that this method can be applied to the metal oxide-hydrogen peroxide system without major changes in the detection limits caused by interferences due to the presence of H₂O₂ and the oxide.

4.2.1 ZrO₂

A study involving determining the amount of CH₂O and consequently the amount of HO• produced during the course of the reaction between H₂O₂ and ZrO₂ was performed. The reaction media consisted of ZrO₂ (4.5 g; Sₐ = 22.5 m²) at T = 293.25 K in 50 ml H₂O with Tris buffer (20 mM) and H₂O₂ (5 mM). The pH was adjusted to 7.5 with HCl. Samples were collected at different time intervals and filtered. Subsequently 1.5 ml of reactant solution was diluted in 2.5 ml solution of ammonium acetate (4 M) and 1 ml solution of
acetoacetanilide (0.2 M) in ethanol. The modified Hantzsch reaction was left to react during 15 minutes at a temperature of 313.15 K. The obtained set of data is represented in Figure 21.

Figure 21. Evolution in the concentrations of H₂O₂ (♦) and CH₂O (■) as a function of reaction time, in the reaction of H₂O₂ with ZrO₂. © American Chemical Society.

According to the proposed overall stoichiometry for the reaction of H₂O₂ in the surface of ZrO₂, Reaction (R15), for each mole of H₂O₂ consumed, two moles of HO• are produced. The measured concentration of HO• represented in Figure 21 is ≈ 1/10 of the concentration predicted by the reaction stoichiometry. This is due to the competition between Tris buffer and H₂O₂ to react with the hydroxyl radical. The energetics of the bonds involved in both reactions are approximately of the same magnitude, the cleavage of the O-H bond in Tris buffer requires around 431 ± 34 kJ·mol⁻¹ of energy, the cleavage of the C-H bond requires 393 kJ·mol⁻¹ while the cleavage of the O-H bond in H₂O₂ requires 429 ± 43 kJ·mol⁻¹. Although the method used for measuring the amount of HO• does not allow discriminating if the HO• are on the surface of the oxide or in solution when scavenged by the Tris, previous studies show that for similar systems, the HO• can be trapped and stabilized on the surface of the metal oxide powder. This could alter the reactivity of these radicals towards Tris and H₂O₂. The rate constant for H₂O₂ decomposition on ZrO₂, obtained in the presence of the HO• scavenging system – Tris/HCl buffer (pH = 7.5) – was compared with the rate constant obtained under normal conditions – no buffering system present (pH = 7.0). The k₁ value obtained for T = 313.15 K under normal conditions is k₁ = (1.22 ± 0.13) x 10⁻⁴ s⁻¹ and the first-order rate constant obtained in the presence of Tris/HCl buffer at pH = 7.5 produced the value k₁ = (1.13 ± 0.70) x 10⁻⁴ s⁻¹. When taking the associated errors into account, the obtained values are in good agreement and it is not possible to state that the buffering system Tris/HCl at pH = 7.5 is affecting the reaction rate when compared to the reaction where no buffer is present.
It can be seen (Figure 21) that the shapes for the curves for disappearance of H$_2$O$_2$ from solution and the corresponding curve for the amount of HO$^*$ scavenged by Tris are symmetrical. This is a strong indication that the scavenged HO$^*$ are a primary product of the decomposition of H$_2$O$_2$ according to Reaction (R11). Also, from the good symmetry of both plots it is possible to state that the processes that lead to the formation of CH$_2$O and its subsequent release into solution have a rate which is in the same order of magnitude as the rate of decomposition of H$_2$O$_2$.

The modified Hantzsch method is an easy and sensitive method for the determination of the concentration of HO$^*$ radicals produced as an intermediate product of the decomposition of H$_2$O$_2$. Given the complexity of the system – due to the possibility of innumerable surface phenomena that could cause interferences with the reaction of production of CH$_2$O and further with the modified Hantzsch reaction – one could expect that the sensitivity of this method would be reduced when applied to the system metal oxide-hydrogen peroxide. This is because of the possible formation of complexes between eventual metal cations released into solution – i.e. from the particles surfaces – and the reagents or products of the modified Hantzsch reaction – i.e. Acetoacetalide, ammonium acetate and the product pyridyl compound. This was not verified and the detection limit for CH$_2$O is in the same order of magnitude of the limit of detection of the method previously published and where no solid was present.

4.2.2 TiO$_2$

In was shown (section 4.1.2.1) that for the reaction of H$_2$O$_2$ with Y$_2$O$_3$ and TiO$_2$, in both cases, after a fast initial disappearance of H$_2$O$_2$ from solution, the reaction is slowed down significantly. To extract the rate constants for adsorption and for decomposition of H$_2$O$_2$, the two kinetic trends were considered to be the result of these two different processes. Verifying if HO$^*$ is formed during the stage of initial fast disappearance of H$_2$O$_2$ from solution is essential in order to make valid statements regarding the surface process involved. The process can either be molecular adsorption of H$_2$O$_2$ onto the surface or decomposition of H$_2$O$_2$ or a mixed adsorption/decomposition phenomenon.

The reaction of H$_2$O$_2$ (5 mM) with TiO$_2$ (0.537 g) was performed in a volume of 50 ml of Tris (20 mM) solution at pH 7.5. The pH was adjusted with HCl. Both the disappearance of H$_2$O$_2$ from solution and the appearance of CH$_2$O were monitored as a function of reaction time. The resulting data is shown in Figure 22.
4 Results and discussion

Figure 22. Evolution in the concentrations of $\text{H}_2\text{O}_2$ (♦) and $\text{CH}_2\text{O}$ (■) during the reaction of $\text{H}_2\text{O}_2$ with a particle suspension of TiO$_2$ at $T = 298.15$ K. © American Chemical Society.

It can be seen (Figure 22) that the initial disappearance of $\text{H}_2\text{O}_2$ from solution is not accompanied by the formation of a detectable amount of HO radicals. From the calibration experiments (Figure 20) a consumption of the equivalent amount of $\text{H}_2\text{O}_2$ (0.5 mM) that disappeared from solution in the initial process of Figure 22 would produce $\approx 0.18$ mM CH$_2$O. Though, it can be seen that no CH$_2$O was detected. Hence, it is possible to conclude that the initial fast disappearance of H$_2$O$_2$ can be attributed to its molecular adsorption onto the surface of TiO$_2$. As the reaction of decomposition of H$_2$O$_2$ proceeds with a constant rate, the rate of formation of CH$_2$O remains fairly constant.

4.2.3 $\text{Y}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{CuO}$, $\text{HfO}_2$, $\text{CeO}_2$ and $\text{Gd}_2\text{O}_3$

The mechanistic study on the formation of HO$^*$ intermediate, was extended to the oxides: Y$_2$O$_3$, Fe$_2$O$_3$, CuO, HfO$_2$, CeO$_2$ and Gd$_2$O$_3$. The data obtained for CH$_2$O formation during decomposition of H$_2$O$_2$ in the presence of Tris is shown in Figure 23.
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Figure 23. Formaldehyde formed by reaction of HO radicals with Tris during decomposition of H₂O₂ (5 mM; 50 mL) catalyzed by different oxides. CeO₂ (■), CuO (*), HfO₂ (▲), Y₂O₃ (●) Gd₂O₃ (×) and Fe₂O₃ (●).

It can be seen (Figure 23) that the dynamics of formation of CH₂O vary considerably for the different oxides. Whilst for Gd₂O₃ the amount of CH₂O formed is very low throughout the whole experiment, reaching a maximum of 0.014 mM, for CuO the amount of CH₂O formed reaches a plateau at slightly above 0.5 mM. For Y₂O₃ the rate of formation is very fast when compared with the other systems. The shape of the curves is also considerably different for the different oxides. The shape of the curves in Figure 23 is dependent on the rate of the reaction of H₂O₂. A way to directly compare the yield of CH₂O for the various oxides in a H₂O₂ decomposition rate independent way is to plot the CH₂O amount as a function of the percentage of H₂O₂ that has been consumed. This plot is show in Figure 24.
Results and discussion

Figure 24. Amount of CH$_2$O present in the reaction system as a function of the percentage of H$_2$O$_2$ consumed from solution during reaction with different oxide materials. CeO$_2$ (♦); Gd$_2$O$_3$ (■); Y$_2$O$_3$ (▲); ZrO$_2$ (×); Fe$_2$O$_3$ (∗); HfO$_2$ (●); CuO (+); TiO$_2$ (−); UO$_2$ (−).

The amount of CH$_2$O produced depends on the amount and also on the relative reactivity of HO• formed in the decomposition of H$_2$O$_2$. One question that can be raised is if the CH$_2$O formed at the oxide interface, has different dynamics of release into solution for the different oxides. This could ultimately lead to differences in CH$_2$O bulk concentration even for the same interfacial/surface concentration. A systematic study on CH$_2$O adsorption onto oxide surfaces – many of them analogues of the oxides investigated here – revealed that CH$_2$O shows a similar adsorption mechanism for different transition and non-transition metal oxides. It is then plausible that the CH$_2$O desorption mechanisms and energy barriers are similar for the different oxides studied here. Besides this fact, in the way that it is expressed, the data of Figure 24 is time-independent in what concerns the formation of CH$_2$O. It is then possible to compare the data directly. It can be seen (Figure 24) that the release of CH$_2$O as a function of H$_2$O$_2$ conversion differs widely for the different oxides. Between some materials, at a given conversion of H$_2$O$_2$, the concentration of CH$_2$O differs by one order of magnitude. The differences observed in Figure 24 can be explained on the basis of the overall mechanism for CH$_2$O formation. Initially, H$_2$O$_2$ in solution is molecularly adsorbed onto the oxide surface. The data presented in section 4.1.2.1 shows that the catalytic decomposition step for ZrO$_2$ is slower than the adsorption for TiO$_2$ and Y$_2$O$_3$. Given this, only minute amounts of HO• are formed during the initial phase (i.e. where the adsorption is the dominating process). As the surface coverage by H$_2$O$_2$
approaches the maximum, the rate of $\text{HO}^\cdot$ formation will also approach its maximum. In aqueous solution the rate constants for the reactions of $\text{HO}^\cdot$ with both $\text{H}_2\text{O}_2$ and Tris differ by two orders of magnitude: $2.7 \times 10^7 \text{ M}^{-1}\cdot\text{s}^{-1}$ and $1.1 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$ for $\text{H}_2\text{O}_2$ and Tris, respectively.\textsuperscript{155,156} In this way, the presence of $\text{H}_2\text{O}_2$ will influence the rate of $\text{CH}_2\text{O}$ formation. In the present case, the reactions occur at the oxide surface and the competition between $\text{H}_2\text{O}_2$ and Tris will depend on the rate constants for the two competing surface reactions as well as the relative surface coverage. Tris, due to its size and geometry will not be able to interact with the surfaces at such a localized level as $\text{H}_2\text{O}_2$. Consequently, its adsorption energy is expected to be less exothermic than that of $\text{H}_2\text{O}_2$. It has been demonstrated that $\text{H}_2\text{O}_2$ has a significantly higher affinity for oxide surfaces than Tris.\textsuperscript{157} For several of the oxides, the formaldehyde production is very low up to a certain conversion of $\text{H}_2\text{O}_2$. The inflection point at which the formaldehyde production rate starts to increase can be attributed to the $\text{H}_2\text{O}_2$ concentration where Tris becomes the dominating reactant at the surface, in terms of its concentration weighted with the rate constant for its reaction with $\text{HO}^\cdot$. Interestingly, the study presented and discussed in section 4.5 of this thesis, on the effects of Tris on the production of molecular oxygen upon catalytic decomposition of $\text{H}_2\text{O}_2$ on $\text{ZrO}_2$ shows that the oxygen yield decreases with increasing Tris concentration. This is a direct consequence of the competition between $\text{H}_2\text{O}_2$ and Tris for hydroxyl radicals. A similar phenomenon was observed in a study of $\text{TiO}_2$ photocatalysis using Tris as a probe and various concentrations of $\text{H}_2\text{O}_2$.\textsuperscript{157} The latter was added to capture electrons formed in the initial photolysis of $\text{TiO}_2$ and thereby enhance the photocatalytic activity. It is interesting to note that for oxides where $\text{H}_2\text{O}_2$ adsorption appears to be faster than the decomposition reaction (e.g. $\text{TiO}_2$ and $\text{Gd}_2\text{O}_3$) a clear inflection point is never reached under the present conditions and very small amounts of formaldehyde are formed. $\text{ZrO}_2$ is a different case where the formaldehyde production starts almost instantly. This could indicate that the adsorption of $\text{H}_2\text{O}_2$ is relatively slow and that catalytic decomposition is a very fast process in comparison. For other more extreme cases such as $\text{HfO}_2$ there is an inflection point when the $\text{H}_2\text{O}_2$ is almost completely consumed from the solution. Tough, for all the materials, it is not possible to attribute the position of the inflection points as the result of a single effect.

For $\text{UO}_2$, the yield of $\text{CH}_2\text{O}$ reaches a plateau corresponding to 20% of $\text{H}_2\text{O}_2$ consumed and in spite of the continuous disappearance of $\text{H}_2\text{O}_2$ from solution, the $\text{CH}_2\text{O}$ amount does not increase. For this material, besides the decomposition, $\text{H}_2\text{O}_2$ is also able to oxidize $\text{U(IV)}$ to $\text{U(VI)}$.\textsuperscript{158} The oxidation product of this reaction is water soluble. As shown previously, the HO radicals produced in the redox reactions are not possible to scavenge with Tris.\textsuperscript{91} The plateau in $\text{CH}_2\text{O}$ production can be interpreted as the point in the
course of the reaction where due to the regeneration of the surface by oxidation of U(IV) to U(VI) – leading to the dissolution of the new formed surface – the contribution of the catalytic decomposition path for the overall H$_2$O$_2$ reactivity will be less.

4.2.4 Kinetic and mechanistic studies of H$_2$O$_2$ reactivity towards UO$_2$ based materials

4.2.4.1 UO$_2$-powder experiments

A mechanistic study on the formation of HO during the reaction of H$_2$O$_2$ with UO$_2$ materials was performed. The reaction media consisted of H$_2$O$_2$, (5 mM), Tris (20 mM), NaHCO$_3$ (1mM) and UO$_2$ powder (0.1 g) in 50 mL H$_2$O. The obtained data is shown in Figure 25.

Overall, for most of the previously discussed oxides – where H$_2$O$_2$ can only react via catalytic decomposition – the dynamics of HO$^\cdot$ formation agree with the dynamics of H$_2$O$_2$ consumption. An interesting question is if for a system where a redox mechanism can also take place, the afore mentioned dynamics are also similar. For the case of the reaction of H$_2$O$_2$ with UO$_2$ powder, the overall reactivity of H$_2$O$_2$ will have a high contribution from a Fenton type of reaction. According to reported dissolution yields, about 80% of the consumed H$_2$O$_2$ will react in a redox process where it oxidizes U(IV) to U(VI). HO$^\cdot$ will also be formed as an intermediate species of this reaction according to Reaction (R9). The remaining 20% of the consumed H$_2$O$_2$ will react via catalytic decomposition also leading to the formation of HO$^\cdot$. The HO$^\cdot$ formed in the oxidation of U(IV) to U(V) is not expected to be scavenged.
4 Results and discussion

by the Tris because the reaction of HO• with U(V) is a very fast process\textsuperscript{159} – the rate constant for reaction of HO• with Tris in aqueous solution is known, but its value for when the reaction takes place at an interface or surface is not known. The scavenged HO• are expected to be produced by the fraction of H\textsubscript{2}O\textsubscript{2} that decomposes catalytically on the surface of UO\textsubscript{2} powder. It can be seen (Figure 25) that a significant amount of HO• are scavenged by Tris. The amount of scavenged HO• corresponds to about 6% of the amount of the H\textsubscript{2}O\textsubscript{2} consumed in the course of the reaction – ZrO\textsubscript{2} this value is of 10%. A rough calculation – using the yield of the method for scavenging HO• from solution – can give an approximate idea of the amount of H\textsubscript{2}O\textsubscript{2} that reacts by decomposition. The resulting fraction of H\textsubscript{2}O\textsubscript{2} that reacts by decomposition is around 17% while the other 83% will react by electron transfer. These values are in excellent agreement with the values estimated for the percentage of H\textsubscript{2}O\textsubscript{2} that reacts by decomposition and by electron transfer. These values were obtained based on the ratio between the amount of dissolved uranium and the amount of consumed H\textsubscript{2}O\textsubscript{2}.\textsuperscript{160} The theory that the radicals formed in the oxidation process cannot be scavenged by the Tris is also supported by these results. Nevertheless this calculation is rather rough as it uses the HO• scavenging yields from solution which might not be applicable to a surface. In the case of UO\textsubscript{2} the HO• scavenging yield from solution is very close to the one at the surface/interface. This indicates that the interactions of the HO• with the surface are weak or the further reactions of HO• are very fast, which causes the HO• formed at the interface to have a lability towards reaction with Tris which is close to that in solution.

\subsection{UO\textsubscript{2} and SIMFUEL pellet experiments}

It is known that the ratio between dissolved uranium and consumed H\textsubscript{2}O\textsubscript{2} – dissolution yield – differs significantly depending if the reaction takes place on pure UO\textsubscript{2}-pellets or SIMFUEL pellets.\textsuperscript{161} SIMFUEL is a material which consists of a UO\textsubscript{2} matrix that has been doped with rare earth elements in order to approximate the material to the real spent nuclear fuel in terms of matrix.\textsuperscript{162} Thus, the fact that a surface reaction shows different kinetic and mechanistic parameters for both materials is expected from elementary surface chemistry concepts, as the inclusion of dopants in a solid leads to the formation of surfaces which are different from the non-doped material, both in terms of their chemical environment but also in terms of their structure.\textsuperscript{163,165}

H\textsubscript{2}O\textsubscript{2} can also react with these materials via a redox process or via catalytic decomposition. It is known\textsuperscript{161} that SIMFUEL displays a much lower dissolution yield than UO\textsubscript{2}. This indicates that for SIMFUEL, a larger fraction of the H\textsubscript{2}O\textsubscript{2} is consumed by catalytic decomposition when compared to UO\textsubscript{2}. The overall reactivity of H\textsubscript{2}O\textsubscript{2} was found to be 50 % lower on SIMFUEL when compared to pure UO\textsubscript{2}. To investigate the mechanistic reasons behind the
observed differences between UO₂ and SIMFUEL the amount of scavenged HO• and dissolved U as a function of reaction time were determined. The presence of the HO• scavenger – Tris – leads to the formation of a soluble complex with U. This complex has its $\lambda_{\text{max}}$ at 340 nm. This fact does not allow for the direct measurement of the H₂O₂ in solution using the Ghormley method ($\lambda_{\text{max}}$ at 350 nm). Though, in these systems, the amount of H₂O₂ consumed in the reaction with the pellets can be determined indirectly. This quantity is related to the amount of uranium in solution – corresponding to the fraction of H₂O₂ consumed in redox reactions – plus half of the HO• produced – corresponding to the fraction of H₂O₂ consumed by catalytic decomposition. It should be noted again that these are rough approximations because it is considered that the yield of the method for HO• determination does not vary between both materials. This might not correspond to reality. It should be also noted that the $S_a$ is significantly lower in the experiments using pellets than in the experiments using powders. Hence, the rate of oxidant consumption will be much lower in the pellet experiment.

The resulting data for the mechanistic experiments on H₂O₂ reactions with UO₂ and SIMFUEL pellets are shown on Figure 26 and Figure 27.

**Figure 26.** Evolution in the concentrations of U(VI) in solution (■) and CH₂O (♦) during the reaction of H₂O₂ with a UO₂ pellet as a function of reaction time at $T = 298.15$ K. The reaction media consisted of a UO₂ pellet in 5 mM H₂O₂, 20 mM Tris-HCl buffer, 1 mM NaHCO₃ in 50 ml H₂O.
It is visible in the data shown in Figure 26 and Figure 27 that significant amounts of hydroxyl radicals are formed during the reaction of H$_2$O$_2$ with both materials. Though, the amount of hydroxyl radical produced is approximately 50 % lower for SIMFUEL than for UO$_2$. This observation is in excellent agreement with the difference in overall reactivity of H$_2$O$_2$ towards these materials. The dissolution yields for UO$_2$ and SIMFUEL pellets are 14% and 0.2 %, respectively. Considering the fact that only the HO• formed in the catalytic decomposition is detectable, it is expected that the amount of scavenged HO• parallel the overall H$_2$O$_2$ reactivity. The electron transfer process has only a minor impact on the H$_2$O$_2$ consumption (14 % for UO$_2$ and 0.2 % for SIMFUEL). The measured uranium concentrations in this work confirm the previous conclusions on the significant difference in dissolution yield between UO$_2$ and SIMFUEL. For SIMFUEL the uranium concentration in solution was close to the detection limit throughout the experiment while for the pure UO$_2$ pellet a significant increase in the concentration of uranium in solution is observed. The ratio between formed HO• and dissolved uranium matches the previously determined dissolution yield. However, the fairly small difference in the amount of HO• scavenged between the two materials supports the idea that the main difference between the materials is the redox reactivity. This is expected because of the inclusion of dopants in SIMFUEL.
4 Results and discussion

4.3 Performance of different density functionals and cluster models in describing the reactivity of H$_2$O$_2$, H$_2$O and HO$^\cdot$ with transition metal oxides.

DFT is a valuable tool for providing a better understanding of the surface chemistry of heterogeneous systems. In this work, the reactivity of H$_2$O$_2$, H$_2$O and HO$^\cdot$ with a multitude of oxide materials was studied using cluster models of the oxides and DFT. For that, various exchange correlation functionals were employed. In this section, the presentation of data (and discussion) is divided in sub-sections by cluster size and degree of surface saturation.

4.3.1 m-(ZrO$_2$)$_{26}$ cluster with B3LYP, B3LYP-D and M06 functionals

A cluster consisting of 26 units of stoichiometric ZrO$_2$ was used to evaluate the adsorption energetics of H$_2$O, H$_2$O$_2$ and HO$^\cdot$. The model was constructed by slicing the extended monoclinic crystal (unit cell parameters (a) 5.143, (b) 5.204, and (c) 5.311 Å, Zr-O bond distance 1.771 Å$^{109}$) and a surface was defined according to the most stable stoichiometric surface of monoclinic zirconia – the ($\bar{1}$$1$$1$) plane.$^{166}$ A top view of the surface of monoclinic ZrO$_2$ structure sliced according to the ($\bar{1}$$1$$1$) plane is shown in Figure 28.

![Figure 28](image.png)

For the study of the reactions at its surface, the cluster geometry was constrained, with the exception of the surface atoms directly involved in adsorption and reactivity of the surface species. This model will be denominated m-(ZrO$_2$)$_{26}$, where m- indicates the monoclinic crystal structure. The m-(ZrO$_2$)$_{26}$ with the highlighted reaction site is shown in Figure 29.
Figure 29. The \textit{m-}(\textit{ZrO}_2)_{26} \textit{cluster} used for the study of adsorption of H\textsubscript{2}O, H\textsubscript{2}O\textsubscript{2} and HO\textsuperscript{*}. The highlighted Zr and O atoms were allowed to relax during geometry optimization of the adsorbed states. Zr (○), O (●). Reproduced by permission of the PCCP Owner Societies.

The choice of this surface site for the study of adsorption was based on preliminary tests that revealed that the adsorption of the species studied here is favored at this surface site when compared to the adsorption at other possible (1\textit{1}1) surface sites. The adsorption energies calculated using the B3LYP and M06 functionals, and the dispersion corrected B3LYP-D, for dissociative and molecular adsorption of H\textsubscript{2}O as well as molecular adsorption of H\textsubscript{2}O\textsubscript{2} and its obtained decomposition products (H\textsubscript{2}O and HO\textsuperscript{*}) are given in Table 5. The obtained geometries are shown in Figure 30.
Figure 30. Obtained geometries for the reactions of H$_2$O$_2$, H$_2$O and HO• on the m-(ZrO$_2$)$_{26}$. a) Dissociative adsorption of 2 H$_2$O; b) molecular adsorption of 1 H$_2$O onto structure a; c) binding of 2 HO radicals onto structure a; d) molecular adsorption of H$_2$O$_2$ onto structure a; d) product of the decomposition of H$_2$O$_2$. Zr (●), O (●), H (○). Bond lengths in Å. Dashed lines represent hydrogen bonds. Note: these are zoomed in images of the products formed at the reaction site highlighted on the cluster shown in Figure 27.
4 Results and discussion

Table 5. $\Delta E_{\text{ads}}$ for adsorption of $\text{H}_2\text{O}$, $\text{H}_2\text{O}_2$ and $\text{HO}^*$ onto a (ZrO$_2$)$_{26}$ cluster. Reaction energy for decomposition of $\text{H}_2\text{O}_2$ ($\Delta E_r$). Values in (kJ·mol$^{-1}$).

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Adsorption energy $\Delta E_{\text{ads}}$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2$\text{H}_2\text{O}$ dissociative</td>
<td>-256 \hspace{1cm} -321 \hspace{1cm} -312</td>
</tr>
<tr>
<td>1$\text{H}_2\text{O}$ molecular$^a$</td>
<td>-109 \hspace{1cm} -139 \hspace{1cm} -132</td>
</tr>
<tr>
<td>2 $\text{HO}^*$ adsorption</td>
<td>-872 \hspace{1cm} -900 \hspace{1cm} -903</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$ molecular</td>
<td>-143 \hspace{1cm} -180 \hspace{1cm} -166</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$ decomposition $\Delta E_r$ $^b$</td>
<td>-523 \hspace{1cm} -513 \hspace{1cm} -520</td>
</tr>
</tbody>
</table>

$^a$ - the adsorption of molecular $\text{H}_2\text{O}$ was studied on the surface of the cluster previously saturated with the products of $\text{H}_2\text{O}$ dissociative adsorption.

$^b$ - the obtained $\text{H}_2\text{O}_2$ decomposition products were based in calculations done on smaller sized cluster models where the transition-states obtained for cleavage of the O-O bond in $\text{H}_2\text{O}_2$ were relaxed (see section 4.3.2 for details on these calculations). The same primary decomposition products were found for this model.

There is an overall good agreement between the data calculated with M06 and B3LYP-D. The highest difference in energies is 14 kJ·mol$^{-1}$. In general, the “dispersion-corrected” functionals B3LYP-D and M06 predict larger adsorption energies than B3LYP. The pure dispersion effect, taken as the difference between B3LYP-D and B3LYP, is between -14 and -37 kJ·mol$^{-1}$, depending on the adsorbed species (ionic, radical, hydrogen bonding). For molecular adsorption of water, the calculated adsorption energies range from -109 kJ·mol$^{-1}$ (B3LYP) to -139 kJ·mol$^{-1}$ (B3LYP-D), which is larger than previously reported DFT values for low surface coverage (Table 6). This is likely a combined effect of using hybrid DFT and dispersion. The energy for dissociative adsorption of water (-312 kJ·mol$^{-1}$ per two water molecules, leading to -156 kJ·mol$^{-1}$ per water molecule with M06,) is in good agreement with experimental data (Table 6), however, there is a large variation in reported experimental data. This is because the experimentally obtained adsorption enthalpies depend on surface coverage and on the surface geometry – i.e. density and type of defects, etc. These in turn depend on the synthetic route used to obtain the surface. Also, the higher exothermicity of the values obtained for adsorption onto this cluster can be attributed to the fact that the clusters terminations are not saturated as in the case of the models that will be discussed next in this work. This causes increased stabilization of the surface atoms of the non-terminated clusters upon
formation of bonds with adsorbates. This is a phenomenon which is known to occur upon formation of bonds with surface sites that are more undercoordinated.\textsuperscript{167} Overall, comparisons between computational and experimental data for water adsorption onto metal oxide surfaces have to be done with care. The metal oxide particles used in the determination of the experimental data were in many cases obtained via different synthetic routes, which produces particles with different surface structure, defects, and anisotropic surface energies.\textsuperscript{168} These discrepancies can have significant influence on the adsorption energies measured using different particles, and differences of 60 kJ·mol\textsuperscript{-1} have been reported for H\textsubscript{2}O adsorption onto two samples of monoclinic ZrO\textsubscript{2} obtained via different synthesis schemes.\textsuperscript{169} Furthermore, the computational data referred in Table 6 was obtained for ideal surfaces sliced according to specific Miller planes. Such models do not take into account effects of defects and the multitude of surfaces present in the real systems. The clusters used herein are intended to model adsorption on rough surfaces or surface defects. This might not be representative of the real system, in which a variety of surface defects are present. Nevertheless, the adsorption energies are within the range of values found in the literature shown in Table 6.
Table 6. Literature data for adsorption of H₂O, HO and H₂O₂ onto ZrO₂, TiO₂ and Y₂O₃. (kJ·mol⁻¹).

<table>
<thead>
<tr>
<th>Type of data</th>
<th>ZrO₂</th>
<th>TiO₂</th>
<th>Y₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O molecular adsorption</td>
<td>-(44 – 150) a²¹⁷⁰</td>
<td>-(48 – 68) a²¹⁷⁵</td>
<td>–</td>
</tr>
<tr>
<td>H₂O dissociative adsorption</td>
<td>-(119; 142) a²¹⁷⁰</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>H₂O₂ molecular adsorption</td>
<td>-(70 – 94) a²¹⁷¹</td>
<td>-(91 – 170) b²¹⁷²</td>
<td>(91) a²¹⁸⁰</td>
</tr>
<tr>
<td>HO• Adsorption</td>
<td>-(110 – 170) a¹⁶⁹</td>
<td>-(22 – 153) b²¹⁷⁶</td>
<td>-(38 – 99) b²¹⁸¹</td>
</tr>
</tbody>
</table>

| **Theoretical** |      |      |      |
| H₂O molecular adsorption | -(42 – 100) b²¹⁷² | -(71 – 79) b²¹⁷⁶ | – |
| H₂O dissociative adsorption | -(194–208) b²¹⁷⁴ | -(90) b²¹⁷⁷ | (91) a²¹⁸⁰ |
| H₂O₂ molecular adsorption | -(91 – 170) b²¹⁷² | -(141) b²¹⁷⁷ | – |
| HO• Adsorption | – | -(4 – 78) b²¹⁷⁹ | – |

<table>
<thead>
<tr>
<th>Type of data</th>
<th>ZrO₂</th>
<th>TiO₂</th>
<th>Y₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O molecular adsorption</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>H₂O dissociative adsorption</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

| **Theoretical** |      |      |      |
| H₂O molecular adsorption | – | – | – |
| H₂O dissociative adsorption | – | – | – |

a) Refers to an ΔH_{ads}; b) refers to an ΔE_{ads} without zero point energy corrections

4.3.2 *m-(ZrO₂)₈* cluster with B3LYP, B3LYP-D and M06 functionals

Another type of cluster to model ZrO₂ surfaces is discussed here. A cluster consisting of 8 ZrO₂ units was constructed in a similar way as the *m-(ZrO₂)₂₆* model. The basis for the usage of the saturated cluster model is the fact that it performs good in cases when the cluster sizes are small.¹⁸²,¹⁸³ For implementing the saturated cluster models, the terminal metal atoms were saturated with hydroxide ions (HO⁻), while terminal oxygen atoms were saturated with protons (H⁺). All the available terminations were saturated with exception for the reactive site in the (1₁₁) plane, where dissociative adsorption of water was investigated. The geometry optimizations were done at the B3LYP/LACVP++ level – for the models described further in this section, all the atoms of the clusters and reacting species were allowed to relax during geometry optimizations. This cluster will from now on be denominated *m-(ZrO₂)₈*. In order to evaluate the effects of dispersion
interactions, adsorption energies were obtained by single-point calculations using the functionals B3LYP, B3LYP-D, and M06. The optimized structure of the \( m-(ZrO_2)_8 \) cluster is shown in Figure 31.

![Figure 31. Optimized geometry of the \( m-(ZrO_2)_8 \) cluster. Zr (●), O (○), H (○). Reproduced by permission of the PCCP Owner Societies.](image)

The obtained Zr-O bond distances are longer than the experimentally observed distances in the crystalline phase (1.771 Å) but are in good agreement with \((ZrO_2)_4\) clusters optimized at the CCSD(T)/aT and B3LYP/aD levels of theory (~2.1 Å). The longer bond distances is due to the lack of a Madelung potential with the same magnitude of the one found in the extended crystal. This causes the bond lengths in the clusters to elongate. Such phenomena also occur upon formation of a surface in a real crystal. A detrimental effect is the one that arises for models such as the \( m-(ZrO_2)_{26} \) shown above. The geometry of the whole cluster was not optimized, with the exception of the reactive site. This means that artificial strain can build up in the cluster atoms and have effects on adsorption and reaction energies obtained with such models. These can be more detrimental than the finite size effects introduced by using a smaller terminated model that has been allowed to fully relax.

The first reaction considered was the dissociative adsorption of H\(_2\)O. The resulting hydroxylated cluster was used then as the starting point for the study of the reactions with H\(_2\)O\(_2\) and HO\(^-\). Dissociative adsorption of water onto the \( m-(ZrO_2)_8 \) model was performed on the atoms: Zr(1), Zr(2), O(1), O(2), O(3), O(4), and O(5) with the resulting HO\(^-\) ions binding to the Zr atoms and H\(^+\) binding to the O atoms. Different adsorption modes of the protons and hydroxide ions from the dissociation of two and four water molecules were considered and compared energetically. The resulting structures obtained for the study of water adsorption are shown in Figure 32 and the corresponding energies are given in Table 7.
Figure 32. Optimized geometries for adsorption of H$_2$O and HO radicals into the different available surface sites of the $m$-(ZrO$_2$)$_8$ cluster: (a), (b), (c) 2 H$_2$O molecules, (d) 4 H$_2$O molecules, (e) 2 H$_2$O molecules and 2 HO radicals, (f) molecular adsorption of H$_2$O (dashed lines represent hydrogen bonds). Zr (●), O (●), H (○). The bond lengths are given in Å. Reproduced by permission of the PCCP Owner Societies.
Table 7. $\Delta E_{ads}$ for adsorption of H$_2$O, HO$^\cdot$ and H$_2$O$_2$ onto the m-(ZrO$_2$)$_8$ model. Activation energy for decomposition of H$_2$O$_2$, with zero point energy corrections ($E_a^{ZPE}$). The respective structures are shown in Figure 32 and 31. Values in kJ·mol$^{-1}$.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Structure</th>
<th>Adsorption energy</th>
<th>B3LYP/ LACV3P++**</th>
<th>B3LYP-D/ LACV3P++**</th>
<th>M06/ LACV3P++**</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 H$_2$O dissociative</td>
<td>Figure 32 (a)</td>
<td>-48</td>
<td>-81</td>
<td>-88</td>
<td></td>
</tr>
<tr>
<td>32 (b)</td>
<td>-77</td>
<td>-107</td>
<td>-120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32 (c)</td>
<td>-61</td>
<td>-90</td>
<td>-92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 H$_2$O dissociative</td>
<td>32 (d)</td>
<td>-156</td>
<td>-240</td>
<td>-241</td>
<td></td>
</tr>
<tr>
<td>2 HO$^\cdot$</td>
<td>32 (e)</td>
<td>-944</td>
<td>-954</td>
<td>-955</td>
<td></td>
</tr>
<tr>
<td>H$_2$O molecular</td>
<td>32 (f)</td>
<td>-71</td>
<td>-85</td>
<td>-78</td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$ molecular</td>
<td>Figure 33 (b)</td>
<td>-36</td>
<td>-61</td>
<td>-46</td>
<td></td>
</tr>
<tr>
<td>$E_a^{ZPE}$</td>
<td>Figure 33 (c)</td>
<td>15</td>
<td>12</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

* - the adsorption of molecular H$_2$O was studied on the surface of the cluster previously saturated with the products of H$_2$O dissociative adsorption.

For dissociative adsorption of 2 H$_2$O molecules, as expected, the most exothermic adsorption mode corresponds to the structure that went through the most extensive adsorption site reconstruction (Figure 32b). On this structure, the O(2) atom initially bound to a Zr lattice atom, was dislocated out of the surface plane. The resulting HO group became bi-bridging between two Zr atoms. Such structures have been reported in both experimental and theoretical studies of dissociative adsorption of H$_2$O in ZrO$_2$ surfaces.$^{186,187}$ The large difference in adsorption energy calculated with B3LYP and B3LYP-D ($\Delta \Delta E_{ads}=30$ kJ·mol$^{-1}$, Table 7) means that dispersion interactions have an important role in adsorption and are necessary to include in the B3LYP functional to improve the accuracy of this functional for calculations on adsorption. The adsorption energies calculated with B3LYP-D (-107 kJ·mol$^{-1}$) and M06 (-120 kJ·mol$^{-1}$), are in reasonable agreement with most experimental data (-70 to -142 kJ·mol$^{-1}$), although larger values (-170 kJ·mol$^{-1}$) have been reported (Table 6). As for the case of the m-(ZrO$_2$)$_{26}$ cluster, B3LYP-D and M06 produce similar data for adsorption.
Dissociative adsorption of four H\textsubscript{2}O molecules, results in a product where the two hydroxyl groups are bound to the already HO coordinated Zr(1) and Zr(2) atoms (Figure 32d). Due to their proximity caused by their increased surface coverage, hydroxyl groups bound to the same Zr atom are stabilized by hydrogen bonding. A similar situation was found when two HO radicals were adsorbed onto a surface site where two H\textsubscript{2}O molecules had previously dissociated (Figure 32e). These observations reveal that the adsorption energies of H\textsubscript{2}O can be highly dependent on the degree of surface coverage due to the existence of cooperative effects in adsorption. These cooperative effects in the case of H\textsubscript{2}O are to a large extent the result of adsorbate-adsorbate hydrogen bonding. For the adsorption of H\textsubscript{2}O, the adsorption of four water molecules (Figure 32d) is the most exothermic. All three functionals predicted this situation, though the adsorption energies obtained with B3LYP-D and M06 are around 85 kJ\cdot mol\textsuperscript{-1} larger than calculated with B3LYP (Table 7). Since the dispersion effect in the adsorption of two water molecules was around -40 kJ\cdot mol\textsuperscript{-1} (Table 7), i.e. roughly half the effect in adsorption of four, it can be concluded that the dispersion effect per water molecule is fairly constant with increasing coverage.

The molecular adsorption of a single H\textsubscript{2}O molecule occurs via hydrogen bonding and covalent interactions between the oxygen atom of H\textsubscript{2}O and the surface Zr(2) atom (Figure 32f). At the B3LYP level, the most stable adsorption mode of two dissociated water molecules (Figure 32b) is only slightly more exothermic than molecular adsorption (Figure 32f, Table 3). On the contrary, the dispersion corrected functionals B3LYP-D and M06 enhances the stability of the dissociative adsorption state significantly, with respect to the state of molecular adsorption. Since the experimental picture is that for ZrO\textsubscript{2} the first water layer dissociates, the dispersion corrected functionals seems to provide a better description. Again, it can be concluded that in these systems, it is necessary to consider the dispersion effects for increasing the accuracy of adsorption data obtained with DFT calculations using B3LYP.

The potential energy surface (PES) for the reaction of decomposition of hydrogen peroxide on the hydroxylated \textit{m-(ZrO\textsubscript{2})\textsubscript{s}} cluster, is illustrated in Figure 33.
Figure 33. Reaction potential energy diagram and optimized structures for the reaction of H$_2$O$_2$ with the surface of the m-(ZrO$_2$)$_8$ cluster: a) cluster after dissociative adsorption of H$_2$O, b) molecular adsorption of H$_2$O$_2$ onto the surface HO groups, c) transition-state for the cleavage of H$_2$O$_2$, d) stable product of the decomposition of H$_2$O$_2$. Zr (●), O (●), H (○). Dashed lines represent hydrogen bonds. Reproduced by permission of the PCCP Owner Societies.

When added to the cluster, the H$_2$O$_2$ molecule adsorbs molecularly onto the surface (Figure 33b). This is in agreement with the experimental data discussed previously in this work which shows that the adsorption of H$_2$O$_2$ is a precedent step to the decomposition. The H$_2$O$_2$ molecule adsorbs by hydrogen bonding with surface HO-groups. In addition to the hydrogen bonds, there are dispersion interactions with the surface atoms, but in this case, B3LYP-D and M06 predict slightly different adsorption energies, $\Delta E_{\text{ads}} = -61$ kJ·mol$^{-1}$ and $\Delta E_{\text{ads}} = -46$ kJ·mol$^{-1}$, respectively.

In the transition state structure (Figure 33c), one of the HO groups of H$_2$O$_2$ is interacting with an exposed Zr cation. When the transition state is relaxed (Figure 33d), the other HO-group of the dissociating H$_2$O$_2$ molecule abstracts a hydrogen atom binding to a surface neighboring O atom. This leads to the formation of water and a surface O•. The existence of the water product is
supported by isotope experiments which show that $\text{D}_2\text{O}$ is formed upon exposure of certain surfaces to $\text{DO}^*$.\textsuperscript{188} The experimentally obtained activation energy is only $33 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$. At the B3LYP level, the activation energy for the cleavage of $\text{H}_2\text{O}_2$ is only $15 \text{ kJ} \cdot \text{mol}^{-1}$, while the barrier obtained with the M06 functional is $32 \text{ kJ} \cdot \text{mol}^{-1}$. Since calculations with B3LYP-D give an activation energy of $12 \text{ kJ} \cdot \text{mol}^{-1}$, the difference between B3LYP and M06 cannot be attributed to dispersion interactions only. Here it is clear that the M06 functional outperforms B3LYP in describing the barrier height, in agreement with the concepts behind the development of the M06 functional.\textsuperscript{124} Spin density isosurfaces obtained with B3LYP and M06 for the transition state geometries are shown in Figure 34.

**Figure 34.** Spin density isosurfaces for the transition state geometries obtained with: a) B3LYP; b) M06 functionals, with LACV3P++** basis set. Alpha-spin density region ( ). Beta-spin density region ( ). Reproduced by permission of the PCCP Owner Societies.

The M06 functional predicts a more localized spin density in the reactive site where $\text{H}_2\text{O}_2$ adsorbs and decomposes. The B3LYP functional predict a more delocalized spin density in comparison. These differences might underline the explanation for the difference in the activation energies obtained with the two functionals. Since the activation energy obtained with the M06 functional is closer to the experimental value than the B3LYP one, it seems reasonable to believe that in the real system the spin density is more localized.

The transition state and formation of products of the $\text{H}_2\text{O}_2$ cleavage is expected to follow a model described by Nilsson and Pettersson\textsuperscript{189} for dissociation of molecular species on catalyst surfaces. This model states that a molecular species undergoes cleavage at a surface due to internal (partial) bond breaking which occur when the interactions with the surface are strong enough to drive this process to completion. The binding of products to the surface starts in the transition state with the formation of a *bond-prepared* radical state where the resulting fragments have unpaired electrons that can interact with available electrons on the catalyst surface. Since the O-O bond in $\text{H}_2\text{O}_2$ is relatively weak ($208 \text{ kJ} \cdot \text{mol}^{-1}$),\textsuperscript{136} compared to the adsorption
4 Results and discussion

energy of the two HO-radicals (-944 kJ·mol⁻¹, Table 7), it is energetically favorable to break the O-O bond and form HO•. The further interaction of the unpaired electron of HO• with the valence electrons of the metal cation leads to formation of bonded states. Besides of incorporating a larger amount of Hartree-Fock exchange (27% in M06, 20 % in B3LYP), the kinetic energy density in M06 is spin dependent,⁶⁴ which can lead to better performance of this functional in describing open-shell systems with unpaired electrons. Also, non-covalent interactions such as hydrogen bonding and van der Waals interactions are important in the reaction of H₂O₂ with the metal oxide. Hydrogen bonds are particularly important in the transition-state for H₂O₂ decomposition. It is known that the M06 functional gives improved results over regular hybrid functionals for describing these types of systems where non-covalent interactions are present and dispersion effects are large.⁶⁴,¹⁹⁰,¹⁹¹

4.3.3 (ZrO₂)₂, (TiO₂)₂ and (Y₂O₃) clusters with B3LYP, B3LYP-D, B3LYP*, M06, M06-L, PBE0, PBE and PWPW91 functionals

The motivation for using the following cluster models of the oxides resides in the fact that for small adsorbates such as the ones studied here, the interactions with a oxide surface are localized.¹⁹² As discussed in the introduction section, in many cases, when defects are present, these defect sites can dictate the overall reactivity of a surface. This means that for such systems, the overall reactivity towards an adsorbate can be determined by localized phenomena. Taking these facts into account, the performance of the minimal possible clusters that retain the stoichiometry of ZrO₂, TiO₂ and Y₂O₃ was investigated. Additionally, the performance of different functionals using these clusters was evaluated. The minimal cluster built for ZrO₂ is shown in Figure 35.
Figure 35. Optimized geometries for adsorption of H$_2$O and further decomposition of H$_2$O$_2$ on a (ZrO$_2$)$_2$ cluster; (a) bare cluster, (b) dissociative adsorption of two H$_2$O molecules, (c) molecular adsorption of a H$_2$O$_2$ molecule, (d) transition-state for the cleavage of the O-O bond in H$_2$O$_2$, (e) product of the decomposition of H$_2$O$_2$. Zr (●), O (●), H (○). The bond lengths are given in Å. Reproduced by permission of the PCCP Owner Societies.

Similar clusters were built for TiO$_2$ and Y$_2$O$_3$. Their structures are shown in Figure 36 and Figure 37 respectively.
Figure 36. Optimized geometries for adsorption of H$_2$O and further decomposition of H$_2$O$_2$ on a (TiO$_2$)$_2$ cluster. (a) bare cluster, (b) dissociative adsorption of two H$_2$O molecules, (c) molecular adsorption of a H$_2$O$_2$ molecule, (d) transition-state for the cleavage of the O-O bond in H$_2$O$_2$, (e) product of the decomposition of H$_2$O$_2$. Ti (●), O (○), H (○). The bond lengths are given in Å. Reproduced by permission of the PCCP Owner Societies.
**Figure 37.** Optimized geometries for adsorption of H$_2$O and further decomposition of H$_2$O$_2$ on a (Y$_2$O$_3$) cluster. (a) bare cluster, (b) dissociative adsorption of two H$_2$O molecules, (c) molecular adsorption of a H$_2$O$_2$ molecule, (d) transition-state for the cleavage of the O-O bond in H$_2$O$_2$, (e) product of the decomposition of H$_2$O$_2$. Y (●), O (●), H (○). The bond lengths are given in Å. Reproduced by permission of the PCCP Owner Societies.

The geometry optimizations were performed with B3LYP and the adsorption and reaction energies were calculated using the functionals B3LYP, B3LYP-D, B3LYP*, M06, PBE0, PBE, PWPW91 and M06-L (Tables 8–10). The geometries for H$_2$O$_2$ decomposition were also optimized using the PBE functional. With this functional, while the water adsorption energies deviate from the B3LYP values with an average of 9 kJ·mol$^{-1}$, the PBE functional predicted a barrierless decomposition of H$_2$O$_2$. 
Table 8. $\Delta E_{ads}$ for adsorption of H$_2$O, H$_2$O$_2$ and HO· onto a (ZrO$_2$)$_2$ cluster. Activation energy with zero point energy correction ($E_a^{ZPE}$) for the decomposition of H$_2$O$_2$ on the surface of the cluster and its respective reaction energy ($\Delta E_r$). Absolute deviation from the experimental value for the activation energy ($D_{exp}$). Values in (kJ·mol$^{-1}$).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP</th>
<th>B3LYP-D</th>
<th>B3LYP*</th>
<th>PWPW91</th>
<th>PBE</th>
<th>PBE0</th>
<th>M06</th>
<th>M06-L</th>
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<tbody>
<tr>
<td>$\Delta E_{ads}$ (2H$_2$O; dissociative)</td>
<td>-229</td>
<td>-261</td>
<td>-230</td>
<td>-218</td>
<td>-209</td>
<td>-233</td>
<td>-258</td>
<td>-231</td>
</tr>
<tr>
<td>$\Delta E_{ads}$ (H$_2$O; molecular)</td>
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<td>-90</td>
<td>-81</td>
<td>-86</td>
<td>-82</td>
<td>-100</td>
<td>-93</td>
<td>-90</td>
</tr>
<tr>
<td>$\Delta E_{ads}$ (2HO·)</td>
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<td>-1023</td>
<td>-1012</td>
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<td>-128</td>
<td>-150</td>
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<tr>
<td>$E_a^{ZPE}$</td>
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<td>34</td>
<td>–</td>
<td>–</td>
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<td>0</td>
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<td>18</td>
<td>9</td>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td>$\Delta E_r$</td>
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<td>-608</td>
<td>-611</td>
<td>-592</td>
<td>-634</td>
<td>-643</td>
<td>-618</td>
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</tbody>
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Note: The functionals PBE, PWPW91 and M06-L predict a barrierless decomposition of H$_2$O$_2$. 
Table 9. $\Delta E_{ads}$ for adsorption of H$_2$O, H$_2$O$_2$ and HO$^-$ onto a (TiO$_2$)$_2$ cluster. Activation energy with zero point energy correction ($E_{a\,ZPE}$) for the decomposition of H$_2$O$_2$ on the surface of the cluster and its respective reaction energy ($\Delta E_r$). Absolute deviation from the experimental value for the activation energy ($D_{exp}$). Values in (kJ·mol$^{-1}$).

<table>
<thead>
<tr>
<th>Note:</th>
<th>B3LYP</th>
<th>B3LYP-D</th>
<th>B3LYP$^*$</th>
<th>PWPW91</th>
<th>PBE</th>
<th>PBE0</th>
<th>M06</th>
<th>M06-L</th>
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<tbody>
<tr>
<td>$\Delta E_{ads}$ (2H$_2$O; dissociative)</td>
<td>-291</td>
<td>-318</td>
<td>-290</td>
<td>-280</td>
<td>-273</td>
<td>-305</td>
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<tr>
<td>$\Delta E_{ads}$ (H$_2$O; molecular)</td>
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<td>-57</td>
<td>-47</td>
<td>-54</td>
<td>-51</td>
<td>-50</td>
<td>-53</td>
<td>-51</td>
</tr>
<tr>
<td>$\Delta E_{ads}$ (2HO$^*$)</td>
<td>-764</td>
<td>-786</td>
<td>-781</td>
<td>-817</td>
<td>-812</td>
<td>-778</td>
<td>-805</td>
<td>-826</td>
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<tr>
<td>$\Delta E_{ads}$ (H$_2$O$_2$; molecular)</td>
<td>-58</td>
<td>-75</td>
<td>-55</td>
<td>-69</td>
<td>-65</td>
<td>-68</td>
<td>-81</td>
<td>-80</td>
</tr>
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<td>$E_{a,ZPE}$</td>
<td>31</td>
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<tr>
<td>$D_{exp}$</td>
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<td>20</td>
<td>59</td>
<td>58</td>
<td>4</td>
<td>6</td>
<td>58</td>
</tr>
<tr>
<td>$\Delta E_r$</td>
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<td>-498</td>
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<td>-489</td>
<td>-513</td>
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functionals PBE, PWPW91 and M06-L predict a barrierless decomposition of H$_2$O$_2$. 
Table 10. $\Delta E_{ads}$ for adsorption of H$_2$O, H$_2$O$_2$ and HO $\cdot$ onto a (Y$_2$O$_3$) cluster. Activation energy with zero point energy correction ($E_{a,ZPE}$) for the decomposition of H$_2$O$_2$ on the surface of the cluster and its respective reaction energy ($\Delta E_r$). Absolute deviation from the experimental value for the activation energy ($D_{exp}$). Values in (kJ·mol$^{-1}$).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP</th>
<th>B3LYP-D</th>
<th>B3LYP*</th>
<th>PWPW91</th>
<th>PBE</th>
<th>PBE0</th>
<th>M06</th>
<th>M06-L</th>
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<tr>
<td>$\Delta E_{ads}$ (2H$_2$O; dissociative)</td>
<td>-172</td>
<td>-182</td>
<td>-170</td>
<td>-170</td>
<td>-119</td>
<td>-174</td>
<td>-192</td>
<td>-187</td>
</tr>
<tr>
<td>$\Delta E_{ads}$ (H$_2$O; molecular)</td>
<td>-70</td>
<td>-79</td>
<td>-71</td>
<td>-69</td>
<td>-65</td>
<td>-77</td>
<td>-76</td>
<td>-79</td>
</tr>
<tr>
<td>$\Delta E_{ads}$ (2HO $\cdot$)</td>
<td>-1081</td>
<td>-1093</td>
<td>-1090</td>
<td>-1098</td>
<td>-1086</td>
<td>-1087</td>
<td>-1099</td>
<td>-1121</td>
</tr>
<tr>
<td>$\Delta E_{ads}$ (H$_2$O$_2$; molecular)</td>
<td>-83</td>
<td>-99</td>
<td>-85</td>
<td>-85</td>
<td>-81</td>
<td>-92</td>
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<td>-95</td>
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<td>$E_{a,ZPE}$</td>
<td>23</td>
<td>28</td>
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<td>–</td>
<td>–</td>
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<td>19</td>
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<td>64</td>
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<tr>
<td>$\Delta E_r$</td>
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<td>-673</td>
<td>-670</td>
<td>-663</td>
<td>-684</td>
<td>-678</td>
<td>-715</td>
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</table>

Note: The functionals PBE, PWPW91 and M06-L predict a barrierless decomposition of H$_2$O$_2$.
Comparing the water adsorption data for the (ZrO$_2$)$_2$ cluster with the m-(ZrO$_2$)$_8$, it can be seen that the adsorption of two H$_2$O molecules on the (ZrO$_2$)$_2$ cluster is more exothermic than for the m-(ZrO$_2$)$_8$ cluster, -260 kJ·mol$^{-1}$ (Table 8) and -120 kJ·mol$^{-1}$ (Table 7), respectively at the M06 level. The most exothermic dissociative adsorption of 2 H$_2$O molecules occurs for adsorption onto the m-(ZrO$_2$)$_{26}$ model, -312 kJ·mol$^{-1}$. These discrepancies are explained with basis on the lower degree of coordination of the Zr atoms in the m-(ZrO$_2$)$_{26}$, followed by the (ZrO$_2$)$_2$ model when compared with the m-(ZrO$_2$)$_8$ cluster. This, as explained before gives the undercoordinated Zr atoms a higher affinity for the HO$^-$ groups which stabilize the shell of the undercoordinated atoms upon adsorption.

Using similar models is possible to compare the differences in adsorption onto the different oxides. The energies for water adsorption onto the ZrO$_2$, TiO$_2$ and Y$_2$O$_3$ minimal clusters follow the trend: $\Delta E_{ads}(Y_2O_3) < \Delta E_{ads}(ZrO_2) < \Delta E_{ads}(TiO_2)$ (Tables 8–10). It is important to recall that upon dissociative adsorption of water, the adsorbates consist on HO$^-$ and H$^+$ which will bind to the metal cation and exposed surface O atoms respectively. The obtained trend can be explained with basis on the local acidity of the metal cation to which the HO$^-$ binds. The 4s and 4p orbital energies of Zr (2$^{nd}$ row transition metal) are higher than the corresponding 3s and 3p orbital energies of Ti (1$^{st}$ row transition metal) because of the higher effective nuclear charge of Ti. Hence the HO$^-$ anion, acting as a Lewis base – donating an electron pair to the metal cation – will form stronger bonds with Ti$^{4+}$ than Zr$^{4+}$. In other words, due to its higher ionization energy and smaller ionic radius,$^{193,194}$ the Ti$^{4+}$ cation in TiO$_2$ is a stronger Lewis acid than the Zr$^{4+}$ cation in ZrO$_2$. The M-O bonds are approximately 100 kJ·mol$^{-1}$ stronger in ZrO$_2$ than in TiO$_2$. Also, the Brønsted acidity of the protonated ZrO$_2$ surface is greater than for the case of the protonated TiO$_2$ surface. In the case of Y$_2$O$_3$, the lower oxidation state (3+) makes the Y$^{3+}$ ions less Lewis acidic than the M$^{4+}$ ions in TiO$_2$ and ZrO$_2$. Consequently, the adsorption of a HO$^-$ group is not as exothermic on Y$_2$O$_3$ as it is for ZrO$_2$ and TiO$_2$. All the functionals used predicted trends for H$_2$O adsorption in agreement with the acid-base concepts described. (Tables 8–10). The only exception is the data obtained with the PBE functional. This predicted a different trend, and systematically produced the less exothermic values for the dissociative adsorption H$_2$O. The most exothermic values for dissociative adsorption of water were systematically obtained with the M06 functional. Again, the M06 and B3LYP-D predict very similar dissociative adsorption energies for H$_2$O. For molecular and dissociative adsorption of H$_2$O, all functionals used – with one exception – predict the dissociative mode to be thermodynamically preferred. The only exception to this is the data obtained with the PBE functional for Y$_2$O$_3$. 


As for adsorption on the \textit{m}-(\textit{ZrO}_2)_8 cluster, the molecular adsorption of \textit{H}_2\textit{O}_2 onto the minimal models is stabilized by hydrogen bonds between \textit{H}_2\textit{O}_2 and the HO groups binding to the metal atoms (Figure 35c, Figure 36c and Figure 37c). The same trend found for molecular adsorption of \textit{H}_2\textit{O} was also found here for \textit{H}_2\textit{O}_2 adsorption. This is in increasing order of exothermicity: TiO\textsubscript{2} < Y\textsubscript{2}O\textsubscript{3} < ZrO\textsubscript{2}. This result is not surprising because the molecular adsorption of both \textit{H}_2\textit{O} and \textit{H}_2\textit{O}_2 occur via a combination of hydrogen bonding and direct interaction with the metal atoms.

The geometry of the transition-state for decomposition of \textit{H}_2\textit{O}_2 in (\textit{ZrO}_2)\textsubscript{2} cluster is slightly different from the corresponding structure obtained in the \textit{m}-(\textit{ZrO}_2)_8 model. The transition state occurs slightly earlier in the smaller model. This is due to the fact that the interactions between \textit{H}_2\textit{O}_2 and the metal cations are less hindered on the smaller model than on the larger model. This could lead to discrepancies on the obtained activation energies. The fact that such effects are also contributing to the reactant structure will cancel to a good extent with the transition-state structure. The obtained $E_{\text{aZPE}}$ with M06 is 32 kJ·mol\textsuperscript{-1} for the \textit{m}-(\textit{ZrO}_2)_8 while for the minimal sized cluster is only 4 kJ·mol\textsuperscript{-1} higher.

The computed dissociation pathway of \textit{H}_2\textit{O}_2 on the \textit{m}-(\textit{ZrO}_2)_8 cluster depends on the exchange-correlation functional used: M06 predicts an activation energy in perfect agreement with experimental kinetic data, B3LYP as well as the dispersion corrected B3LYP-D functional, underestimate the activation energy by 15 kJ·mol\textsuperscript{-1}. In order to understand this difference a variety of exchange-correlation functionals of different types where employed for the calculation of the energy barrier using the minimal sized clusters. Although the functionals applied differ in several ways (see further the computational details section) there is a correlation between the amount of HF exchange included in the exchange-correlation functional and the accuracy of the functional for reproducing the experimentally obtained values. For dissociation of \textit{H}_2\textit{O}_2 on (\textit{ZrO}_2)\textsubscript{2}, the hybrid functionals (B3LYP, B3LYP*, B3LYP-D, M06 and PBE0) predict activation energies between 33 and 42 kJ·mol\textsuperscript{-1} (Table 8), which are in reasonable agreement with the experimental value 33± 1 kJ·mol\textsuperscript{-1} (Table 4). The density functionals that do not incorporate HF exchange (PW91, PBE, and M06-L) predict an activation energy of only 15 kJ·mol\textsuperscript{-1}. For dissociation on (\textit{TiO}_2)\textsubscript{2} the results of pure functionals get worse. While the activation energy for decomposition calculated with hybrid functionals (B3LYP, B3LYP-D, M06 and PBE0) deviate from the experimental value (37± 1 kJ·mol\textsuperscript{-1}, Table 4) by 6 kJ·mol\textsuperscript{-1} or less (Table 9), pure density functionals (PBE and M06-L) were unable to predict an energy barrier for decomposition of \textit{H}_2\textit{O}_2. The re-parameterized hybrid functional B3LYP*, which incorporates 15 percent HF exchange instead of the 20 percent in the original B3LYP functional, is an outlier in the prediction of
activation energies. Although it predicts an energy barrier for decomposition of H$_2$O$_2$, the deviation from the experimental data is larger than for the other hybrid functionals employed (error of 20 kJ·mol$^{-1}$). Similar trends were obtained for decomposition on Y$_2$O$_3$. Here pure DFT also predicted a barrierless reaction (Table 10). Given this, it is plausible to state that in order to correctly describe the energy barrier for H$_2$O$_2$ decomposition, the functional used should incorporate an amount of HF exchange of at least 20 percent. Among the three functionals that incorporate HF exchange, the M06 and PBE0 performed better than the B3LYP in terms of reaction energy barriers accuracy. The activation energies calculated with M06 deviate from experiment by 6 kJ·mol$^{-1}$ on average absolute value, while the deviation for PBE0 is 5 kJ·mol$^{-1}$, and B3LYP deviates with 12 kJ·mol$^{-1}$. Given the very good agreement between computational and experimental data for the energy barriers for H$_2$O$_2$ decomposition, it is possible to state that the minimal models constitute a simple and effective approach for modeling reactivity of particles of these oxides and H$_2$O$_2$.

The calculated reaction energies for H$_2$O$_2$ decomposition, are in good agreement with the trend verified for the HO• adsorption energies (Table 8–10). The reasoning for this is that the products formed in the decomposition of H$_2$O$_2$ consist of a H$_2$O molecule molecularly adsorbed to the clusters and a HO radical bound to one of the metal atoms. When comparing the reaction energies for the different clusters, the factor that is expected to have more impact on the overall reaction energy is the adsorption of HO• onto the clusters given that this quantity is far larger than the molecular adsorption energy of a H$_2$O molecule (Tables 8–10). Even though the HO radical binds strongly to all three metal oxides, the formation of H$_2$O as a product of decomposition of H$_2$O$_2$ is supported by experiments which show that HO• can react further at a solid/liquid interface.$^{197}$

Since dispersion interactions occur not only through bonds but also through space, the cluster size (and geometrical shape) has an impact on the magnitude of the dispersion effect on the calculated adsorption energy. Taking the difference between adsorption energies calculated with B3LYP and B3LYP-D as the dispersion effect, it can be seen that for the molecular adsorption of water on ZrO$_2$ clusters, the dispersion effect is only 10 kJ·mol$^{-1}$ in the (ZrO$_2$)$_2$ model (Table 8), while is 14 kJ·mol$^{-1}$ in the $m$-(ZrO$_2$)$_8$ model (Table 7) and becomes as large as 30 kJ·mol$^{-1}$ in the $m$-(ZrO$_2$)$_{26}$ cluster (Table 5). Differences of similar magnitude are found for the molecular adsorption of H$_2$O$_2$.

### 4.4 Affinity of ZrO$_2$, TiO$_2$ and Y$_2$O$_3$ for the HO radical

In the mechanistic studies described in section 4.2 there are a multitude of processes which determine the differences in the yield of CH$_2$O for the
different oxides. To consider, there are: the adsorption of H$_2$O$_2$ and Tris onto the surfaces, the reactivity of both species towards the HO radical and the reactivity of the HO radical towards the surfaces. From the properties of the surfaces and the similarities in H$_2$O$_2$ adsorption energies (Section 4.3), it is expected that for oxides of transition metals that are neighbors in the periodic table, there should not exist extreme differences in the parameters mentioned above with the exception of the HO radical binding energies (See section 4.6.2). As such, the scavenging capability of the different metal oxides towards HO$^\cdot$ present in solution was investigated. This was done by γ-irradiating aqueous powder suspensions of the different oxides in the presence of Tris and determining the amount of CH$_2$O formed – in a similar way as to what was done for the study of the formation of HO$^\cdot$ during the catalytic decomposition of H$_2$O$_2$. The competition for HO$^\cdot$ between Tris and the surface of the oxides can give a picture of the differences in the abilities of the different oxides to scavenge HO$^\cdot$ from solution. The reaction media for the study of the affinity of the oxides for HO$^\cdot$, consisted of ZrO$_2$ (1.5 g, $S_a = 7.5$ m$^2$) or TiO$_2$ (0.197 g, $S_a = 7.5$ m$^2$) or Y$_2$O$_3$ (1.678 g, $S_a = 7.5$ m$^2$) in Tris (20 mM) and a volume of 50 ml. The plots showing the amount of HO$^\cdot$ scavenged by Tris, as a function of irradiation time are represented in Figure 38.

![Figure 38](image_url)

**Figure 38.** Accumulated [HO$^\cdot$] scavenged by Tris in γ-irradiated solutions with and without the presence of different metal oxides. No oxide present (♦); TiO$_2$ (▲); ZrO$_2$ (■); Y$_2$O$_3$ (●). © American Chemical Society.

From Figure 38 it can be seen that the different metal oxides display different yields of scavenged HO$^\cdot$. As discussed above, this fact can provide a qualitative measure of the binding energy of HO$^\cdot$ to the surfaces of the oxides. The strengths of these bonds are expected to control the relative kinetics for adsorption, desorption and eventual diffusion of HO$^\cdot$ on the surface.$^{198}$ According to the plots of Figure 38, the HO$^\cdot$ binding energies vary in the order of increasing exothermicity: TiO$_2$ < ZrO$_2$ < Y$_2$O$_3$. Also important
to note is that the amount of HO• scavenged from solution by the metal oxide depends on the \((S_a/V)\) of the metal oxide present in the system. The amount of HO• scavenged varies inversely with metal oxide \((S_a/V)\).

The DFT obtained geometries for the binding of two HO radicals onto the hydroxylated clusters of \((\text{ZrO}_2)_2\), \((\text{TiO}_2)_2\) and \((\text{Y}_2\text{O}_3)\) are shown in Figure 39. The corresponding energetic data are given in Table 8–10. A Mulliken population analysis shows that the adsorption of HO• causes delocalization of electrons of the metal atoms involved in the bonding with HO•, i.e. the metal cation becomes partially oxidized. This could be seen systematically on the Mulliken charges of the metal atoms for all the models studied. The adsorption energies of HO• can be reasoned in terms of the ionization energy of the metal cation binding with the radicals. The ionization energies of the metal ions present in the oxides vary in the order: \(\text{Y}^{3+} < \text{Zr}^{4+} < \text{Ti}^{4+}\). As delocalization of the metal valence electrons has to occur in order to form bonded states with the HO radicals, the strength of the bonds between the metal clusters and the HO radicals is expected to follow the inverse trend as the ionization energies. This because the ionization energy is inversely proportional to the ease of delocalization of electronic density from an atom.

This trend was successfully reproduced with all the exchange-correlation functionals used (Table 8–10) and agrees with the experimental data shown in Figure 38. Thus, the higher the ionization energy of the metal cation present in the cluster, the smaller is the change in Mulliken charge of the metal atom upon adsorption of HO•.

![Figure 39](image)

**Figure 39.** Optimized geometries for the adsorption of two HO radicals onto each of the clusters previously saturated with two H₂O molecules: (a) \((\text{ZrO}_2)_2\), (b) \((\text{TiO}_2)_2\), (c) \((\text{Y}_2\text{O}_3)\). Zr (●), Ti (●), Y (●), O (●), H (○). © American Chemical Society.

A similar trend to the one here obtained has been previously reported for adsorption of HO• onto metallic Au surfaces.\(^93\) The authors found that the lower the oxidation potential of a given Au surface, the stronger the bonds between that surface and HO•. This also indicates that for a metallic surface,
the formation of bonds with HO• requires delocalization of electron density from the metal atom.

4.5 Effect of HO• scavengers on the mechanism of decomposition of H₂O₂

It has been show with the experimental mechanistic data for H₂O₂ decomposition, with the DFT calculations of the mechanism of decomposition of H₂O₂ and with the experiments and calculations of the affinity of the oxides for HO•, that this radical might have an important role in the mechanism of decomposition of H₂O₂.

In surface reactions, changing the amount of an intermediate surface species has consequences on the overall reaction mechanism. Rewriting Reaction (R11) according to the experimental and DFT finds described previously in this work

\[ \text{H}_2\text{O}_2 \,(\text{ads}) + S_{CA} \rightarrow \text{H}_2\text{O} \,(\text{ads}) + \text{HO}^* \,(\text{ads}) + S_{CA}^* \]  
\[ \text{H}_2\text{O}_2 \,(\text{ads}) + \text{HO}^* \,(\text{ads}) \rightarrow \text{H}_2\text{O} \,(\text{ads}) + \text{HO}_2^* \,(\text{ads}) \]  
\[ \text{H}_2\text{O}_2 \,(\text{ads}) + S_{CA}^* \rightarrow \text{HO}_2^* \,(\text{ads}) + S_{CA}\text{H} \]  
where (ads) represents an adsorbed state and \( S_{CA}^* \) is the surface catalytically active site with the unpaired electron at the O atom (Figure 33d, Figure 35e and Figure 37e). The non-adsorbed or weakly adsorbed HO• can eventually react with H₂O₂ according to

\[ 2\text{H}_2\text{O}_2 \,(S_{CA}) \rightarrow 2\text{HO}_2^* \,(S_{CA}) + 2\text{H}^* \,(S_{CA}) \rightarrow 2\text{HO}_2^* \,(S_{CA}) + \text{H}_2 \,(\text{g}) \]  
where the state \( S_{CA} \) denotes that the corresponding species is adsorbed onto the surface catalytically active site. It has been shown in section 4.3 that H₂O₂ binds to the \( S_{CA} \) site by direct interaction of its O atoms with undercoordinated metal cations at the surface. A similar type of interaction happens for the binding of the HO radicals. These two types of interactions are similar in the sense that both require access to the orbitals of the metal cations in order to form bonded states. So both the H₂O₂ and HO• interactions with the surfaces, are more exothermic, the more undercoordinated are the metal cations to which these species bind. As such, the adsorption of H₂O₂ would be facilitated by the removal of HO• entities from the system because adsorbed HO• competes with H₂O₂ for adsorption.
onto exposed surface metal cations. In this section, the effects of HO• scavengers – Tris and TAPS – on the products of the decomposition of H2O2 when catalyzed by ZrO2, TiO2 and CuO, are presented and discussed.

In order to correctly evaluate the effects on the mechanism of decomposition of H2O2 due to scavenging HO• by Tris and TAPS, it is necessary to know the adsorption equilibrium constants of these compounds onto the surfaces. This in order to qualitatively know which of these scavengers has a higher surface concentration. The adsorption equilibrium constants for Tris and TAPS were determined for the ZrO2 system. Upon exposure of a 5 ml solution of varying concentration of Tris or TAPS (100-500 μM, V = 5 ml) to ZrO2 (2.5 g, Sa = 12.5 m²) at pH = 7.5, the amount of Tris and TAPS adsorbed onto the surface at equilibrium was determined from the γ-radiation induced bleaching of the methylene blue. This method measures the competition kinetics between methylene blue and Tris or TAPS for the radiation induced produced HO• radicals. Methylene blue reacts with HO• radicals with a rate constant of 6.9 × 10¹⁰ M⁻¹·s⁻¹. The rate constant for reaction of Tris with HO• radicals is 1.1 × 10⁹ M⁻¹·s⁻¹. The rate constant for the reaction of TAPS with HO• radicals has not been precisely determined but based on structural factors – i.e. structural similarities between TAPS and other Good’s buffers – it is expected to be on the order of 10⁹ M⁻¹·s⁻¹. From these rate constants it can be seen that the optimal conditions for the competition kinetics are for a concentration of Tris or TAPS around 10 times higher than the concentration of methylene blue. The resulting data for the percentage of adsorbed Tris and TAPS at equilibrium as a function of their initial concentrations are represented in Figure 40.

**Figure 40.** Percentage of Tris (♦) and TAPS (■) adsorbed at equilibrium as a function of their initial concentration in solution at pH = 7.5 for adsorption onto ZrO2 (2.5 g) at 298 K in a V = 5 ml.

From Figure 40 it can be seen that at equilibrium, TAPS has a higher surface concentration than Tris for the same initial solution concentration. According
to the Langmuir theory of adsorption, the adsorption at equilibrium conditions can be expressed by

$$q_e = \frac{x_m \cdot k \cdot C_e}{1 + k \cdot C_e}$$  (15)

where $q_e$ is the amount of adsorbate adsorbed per unit weight of adsorbent, $x_m$ is the amount of adsorbate required for a monolayer coverage on the surface of the adsorbent, $K$ is the Langmuir adsorption equilibrium constant and $C_e$ is the equilibrium concentration of adsorbate in solution. The Langmuir adsorption equilibrium constant, $K$, is defined as $k_d/k_a$ where $k_d$ and $k_a$ are the rate constants of adsorption and desorption. The linearization of Equation (15) has the form

$$\frac{1}{q_e} = \frac{1}{x_m} + \left(\frac{1}{K \cdot x_m}\right) \left(\frac{1}{C_e}\right)$$  (16)

the quantity $K$ as defined above can give a comparative picture of the differences in terms of surface coverage and adsorption energies for both molecules and can be obtained by plotting $1/q_e$ as a function of $1/C_e$. The value of $K$ for Tris is $2.5 \times 10^{-3}$ and for TAPS is $4.6 \times 10^{-4}$. Hence, from these data can be seen that the adsorption of TAPS is more exothermic than adsorption of Tris. Translated into the adsorption mechanism, these adsorption data suggests that the area of the surface of ZrO$_2$ covered, is 4.5 times higher when the adsorbate is TAPS than for the case when the adsorbate is Tris – for the same initial concentration of adsorbate.

To study the effect of HO$^\cdot$ scavengers on the mechanism of H$_2$O$_2$ decomposition on the surface of ZrO$_2$, the gaseous products H$_2$ and O$_2$ formed upon decomposition of H$_2$O$_2$ in the presence of varying amounts of the HO$^\cdot$ scavengers Tris or TAPS was measured. During H$_2$O$_2$ decomposition, O$_2$ is formed according to Reaction (R14).$^{129}$ According to the Reaction (R20) the eventual formation of H$_2$ can also take place.

Prior to the measurement of the gaseous products, test experiments were performed to ensure complete consumption of H$_2$O$_2$ when the reaction products were measured. Before the analysis of the amount of H$_2$ and O$_2$ formed as a function of HO$^\cdot$ scavenger concentration, several background experiments were performed. The reaction media for the background experiments consisted of one of the HO$^\cdot$ scavengers, either Tris or Taps (200 mM) in a ZrO$_2$ particle suspension without H$_2$O$_2$ present. When H$_2$O$_2$ is not present in the reaction media, there is no detectable production of H$_2$. The amount of H$_2$ produced was studied for varying concentrations of HO$^\cdot$ scavengers and also for different concentrations of H$_2$O$_2$ at a fixed concentration (200 mM) of HO$^\cdot$ scavenger. The resulting data for the later experiments are shown in Table 11.
Table 11. H$_2$ detected (mM) after reaction of H$_2$O$_2$ in a ZrO$_2$ particle suspension as a function of the different amounts of H$_2$O$_2$ at a fixed concentration (200 mM) of Taps or Tris.

<table>
<thead>
<tr>
<th>[H$_2$O$_2$] (mM)</th>
<th>[H$_2$] detected (mM)</th>
<th>[H$_2$] detected (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(in Taps (200 mM))</td>
<td>(in Tris (200 mM))</td>
</tr>
<tr>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.0</td>
<td>$1.6 \times 10^{-5}$</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>$2.0 \times 10^{-2}$</td>
<td>$1.7 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

It can be seen (Table 11) that the amount of H$_2$ formed is dependent on the amount of H$_2$O$_2$ present in the system. For the lower concentration of H$_2$O$_2$ used (0.2 mM), there is no detectable formation of H$_2$.

The study of the formation of H$_2$ as a function of HO$^\bullet$ scavenger concentration was done for a system of ZrO$_2$ particles (0.4 g; $S_a = 1.34$ m$^2$) with H$_2$O$_2$ (10 mM) and varying concentrations of Tris and Taps in a volume of 2 ml. The choice of this concentration of H$_2$O$_2$ was based on the results of the test experiments shown in Table 11. The data obtained are represented in Figure 41 and Figure 42 for Tris and TAPS, respectively.

**Figure 41.** Production of O$_2$ (■) and H$_2$ (♦) in the decomposition of H$_2$O$_2$ on the surface of ZrO$_2$ in the presence of different concentrations of the HO$^\bullet$ scavenger Tris (0-0.2 M).
4 Results and discussion

**Figure 42.** Production of O$_2$ (■) and H$_2$ (♦) in the decomposition of H$_2$O$_2$ on the surface of ZrO$_2$ in the presence of different concentrations of the HO$^*$ scavenger Taps (0-0.2 M).

In the experiments without HO$^*$ radical were detected amounts of O$_2$ that are in agreement with the proposed stoichiometry for the decomposition of H$_2$O$_2$. The amount of O$_2$ formed is equal to half of the initial amount of H$_2$O$_2$, according to Reaction (R14). The results presented in Figure 41 and Figure 42, show that the presence of an HO$^*$ radical scavenger – either Tris or Taps – has an effect on the amounts of O$_2$ and H$_2$ produced by the decomposition of H$_2$O$_2$. The total amount of O$_2$ is reduced and that of H$_2$ is increased. Both the decrease in O$_2$ and the increase in H$_2$ are proportional to the amount of HO$^*$ scavenger in the system. For the system where the scavenger is Tris (Figure 41) this is visible for concentrations of Tris higher than 75 mM. The difference in how the two scavengers affect the O$_2$ yield is noticeable at scavenger concentrations above 0.08 M. For Tris, the decrease in O$_2$ yield becomes less pronounced for scavenger concentrations higher than 0.08 M, while the O$_2$ yield decreases linearly up to 0.2 M of TAPS. The changes in the yield of H$_2$ with increasing concentration of scavenger are also visible. For the same initial solution concentrations, the production of H$_2$ is higher when TAPS is present than for the case of Tris. According to the adsorption experiments, the surface coverage is 4.5 times higher when TAPS is the adsorbate when compared with the adsorption of Tris, for the same initial solute concentration. This implies that at the surface/interface, TAPS is able to scavenge more HO$^*$ than Tris due to its higher surface/interfacial concentration. This is in agreement with the change in yields of the gaseous products observed Figure 41 and Figure 42 and suggests that the formation of H$_2$ is a surface process that depends on the presence and on the surface coverage of an HO$^*$ scavenger. This reasoning is further supported by test experiments using TiO$_2$ and CuO. As for the case of ZrO$_2$, for these systems,
the presence of Tris or Taps has similar effects on the H$_2$ and O$_2$ yields (Table 12).

**Table 12.** Yields (M) of H$_2$ and O$_2$ for the reaction of decomposition of H$_2$O$_2$ (10 mM) catalyzed by CuO or TiO$_2$ in the presence of the HO$^*$ scavengers Tris or Taps (0.2 M).

<table>
<thead>
<tr>
<th>HO$^*$ scavenger</th>
<th>CuO – O$_2$</th>
<th>CuO – H$_2$</th>
<th>TiO$_2$ – O$_2$</th>
<th>TiO$_2$ – H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No scavenger</td>
<td>5.0 × 10$^{-3}$</td>
<td>0</td>
<td>5.0 × 10$^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>Tris (0.2 M)</td>
<td>2.7 × 10$^{-3}$</td>
<td>8.4 × 10$^{-6}$</td>
<td>1.0 × 10$^{-4}$</td>
<td>9.3 × 10$^{-6}$</td>
</tr>
<tr>
<td>TAPS (0.2 M)</td>
<td>1.2 × 10$^{-3}$</td>
<td>1.6 × 10$^{-5}$</td>
<td>8.9 × 10$^{-4}$</td>
<td>3.0 × 10$^{-5}$</td>
</tr>
</tbody>
</table>

When no scavenger is present, the amount of O$_2$ detected corresponds to the amount of this product predicted by the overall stoichiometry for H$_2$O$_2$ decomposition for a system where no HO$^*$ scavenger is present – Reaction (R14). For the reaction media where Tris or Taps are present, the yields of both O$_2$ and H$_2$ are shown in Table 12. For the same: $S_a$ of solid, [H$_2$O$_2$]$_0$ and [Tris or Taps], the yields of H$_2$ and O$_2$ for CuO and TiO$_2$, (Table 12) are different than for the case of ZrO$_2$, but the same trends are found. The presence of a HO$^*$ scavenger enhances the formation of H$_2$ and decreases the yield of O$_2$.

For all oxides, when using TAPS or Tris, the changes in the production of O$_2$ and H$_2$ do not seem to obey a specific mass balance. Nevertheless, it is demonstrated that the presence of a HO$^*$ scavenger influences the overall H$_2$O$_2$ reaction path. The presence of a HO$^*$ scavenger favors a reaction which leads to formation of H$_2$ and at the same time affects the main reaction path that leads to the formation of O$_2$. This observation further illustrates the importance of the HO$^*$ radical as an intermediate reactive species on the decomposition of H$_2$O$_2$. As shown in sections 4.2 and 4.3 of this thesis, HO$^*$ is a primary product of H$_2$O$_2$ decomposition and it competes with H$_2$O$_2$ for the same adsorption sites at the surface of the metal oxides. Removal of the HO$^*$ from the reaction system has an effect on the relative yields of the products formed. Without the HO$^*$ scavenger, H$_2$O$_2$ decomposes at the surface of the oxides according to the following stoichiometric relationship stated in Reaction (R14): 1 mole of H$_2$O$_2$ forms $\frac{1}{2}$ mole of O$_2$ and 1 mole of H$_2$O. The presence of the HO$^*$ scavenger changes the overall mechanism to a scheme that can be illustrated by
this reaction can be explained in terms of the increase in yield of a side reaction such as the one represented in Reaction (R20). A determination of the coefficients $x$, $y$ and $z$ is not trivial since their values depend on many parameters besides the solution concentration of an HO• scavenger.

The removal of HO• from the SCA site is expected to contribute in two distinctive ways to the formation of H2. The first is that the increased removal of HO• from the surface facilitates the adsorption of H2O2 through direct interaction of its O atoms with the metal cations. This exchange will lead to a higher H2O2 coverage at the SCA sites. According to the stoichiometry of the proposed Reaction (R20), this reaction would benefit from a higher coverage of H2O2 at the SCA sites. The other contribution is that the alternative reactive pathway of H2O2 decomposition by breaking one of the H-O bonds is also enhanced because there is room at the SCA site to accommodate the resulting products, the HO2• and H• radicals. Surface adsorption of H• is known to occur for ZnO and the surface migration of adsorbed H• can have an activation energy as low as 38 kJ·mol$^{-1}$. For metallic surfaces of Cu, H• adsorbed on neighboring surface metal atoms can easily recombine to form H2. A similar type of surface adsorbed H radical recombination is expected to occur at the surfaces of the oxides here examined. This recombination has been shown to be possible at surface sites where the adsorbed H atoms are bound to neighboring atoms as reported for TiO2 surfaces.

4.6 Application of conceptual DFT to derive catalyst structure-reactivity relationships for the decomposition of H2O2

4.6.1 PBE0 functional study of the decomposition of H2O2 on clusters of Fe2O3; Al2O3; CuO; CeO2; HfO2; NiO2; PdO2; TiO2; Y2O3; ZrO2; Gd2O3

In this section, the DFT calculations for decomposition of H2O2 are extended for a total of 9 oxides and the adsorption energies of HO• radicals onto the hydroxylated clusters of a total of 11 oxides are investigated. The tools of conceptual DFT (Section 2.5) are here applied to experimental data to derive structure-activity relationships for decomposition of H2O2 for the oxides: Fe2O3; Al2O3; CuO; CeO2; HfO2; NiO2; PdO2; TiO2; Y2O3; ZrO2; Gd2O3. The same methodologies described in Section 4.3 are applied in this section. Here, the functional PBE0 was used for all geometry optimizations and calculations of the single point energies. This functional revealed faster than the B3LYP and more robust for the location of the transition-states. Also for the lanthanide oxides the B3LYP functional has shown difficulties in locating the transition-states for H2O2 decomposition. Due to the very good performance/computational effort ratio, achieved by using these models, the
clusters used for this study were again based on the smallest possible stoichiometric units of the metal oxides described in Section 4.3.3. These are of the type $(M_xO_y)_n$, where $M$ is the metal oxide cation and $n$ is the number of stoichiometric units of the metal oxide. The values of $n$ are 1 or 2 depending on if the oxide is of the type $M_2O_3$ or $MO_2$ respectively. These clusters were then further hydroxylated with the products of $H_2O$ dissociative adsorption – (HO$^-$) and (H$^+$) binding to the cation and to the O atoms respectively. This procedure decreases the coordinative unsaturation of the models which leads to a more realistic modeling of the surfaces of the oxides in solution. This phenomenon also leads to a decrease in the coordinative unsaturation of the exposed surface atoms. In order to maintain a charge neutral system, the clusters of the oxides of the type $M_2O_3$ reacted with the products of dissociation of one water molecule and the clusters of the type $MO_2$ have reacted with those of two water molecules. The resultant products of these reactions with water are the initial reactants for the study of the reactivity of $H_2O_2$ and are shown in Figure 43.
4 Results and discussion

<table>
<thead>
<tr>
<th>Al₂O₃</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>CeO₂</td>
</tr>
<tr>
<td>HfO₂</td>
<td>NiO</td>
</tr>
<tr>
<td>PdO₂</td>
<td>TiO₂</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>ZrO₂</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 43.** Structures of the hydroxylated clusters used to study the adsorption and further decomposition of H₂O₂. The clusters consist of stoichiometric units of the mentioned oxides, where H₂O has been dissociatively adsorbed. Metal (☉), O (☉), H(O).

The most stable spin states were found to be the singlet, with the exceptions of CuO-quintet and Fe₂O₃-eleventh. During the course of the reactions investigated here, no spin crossover was found for these clusters. In Figure 43 can be seen that the oxides of the transition metal elements belonging to the same periodic table group have a tendency to form similar structures upon dissociative adsorption of H₂O. For example, the hydroxylated clusters of the oxides of Ti(IV), Zr(IV) and Hf(IV) (elements of the group IV) show structural similarities among them in what concerns the way the HO⁻ groups bind to the structures. Ni(IV) and Pd(IV) (elements of the group X) also form similar structures upon the dissociative adsorption of H₂O. For clusters of
different stoichiometry such comparisons on water adsorption geometries are unfeasible.

In the mechanisms described in Section 4.3.3, for ZrO₂, TiO₂ and Y₂O₃, the obtained first step of the decomposition of H₂O₂ is the molecular adsorption. Analogously, for all oxides, a first energy minimum corresponding to the molecular adsorption of H₂O₂ was found. The investigation of the energy barriers for cleavage of H₂O₂ was done only for the oxides for which there are coherent experimental data to compare with. The resulting geometries for adsorption of H₂O₂ onto CeO₂, CuO, Fe₂O₃, HfO₂ and Al₂O₃ are shown in Figure 44. The structures of ZrO₂, TiO₂ and Y₂O₃ are here omitted because there were no significant differences between the PBE0 geometries here obtained and the B3LYP structures shown in Section 4.3.3.

As described for the previous oxides studied, in order to form the molecular adsorption structure, H₂O₂ binds to the clusters by direct interaction of its O atoms with the oxide metal cation. Another type of interaction present is hydrogen bonding, and for all oxides, H₂O₂ acts both as a donor and acceptor. From these structures (Figure 44), H₂O₂ undergoes decomposition. The obtained structures of the transition-states for the decomposition of H₂O₂ are shown in Figure 45. The reaction energy barriers are given in Table 13.
Figure 45. Transition-states for the decomposition of H$_2$O$_2$ catalyzed by hydroxylated clusters of CeO$_2$, CuO, Fe$_2$O$_3$, HfO$_2$, Al$_2$O$_3$. Metal cation (●), O (●), H(●).

The transition-states obtained are similar for all the oxides. The decomposition of H$_2$O$_2$ consists of a first molecular adsorption step followed by the cleavage of its O-O bond. The only exception is Fe$_2$O$_3$. For this cluster, the decomposition of H$_2$O$_2$ follows a transition-state involving the cleavage of the H-OOH bond. This reaction has been discussed in the literature as a possible pathway for the decomposition of H$_2$O$_2$. Though, due to the higher BDE and consequent energy barrier for the cleavage of the H-OOH bond when compared with the O-O bond, this is expected to be a side reaction and not the main reaction path. This was observed for all oxides studied so far with the minimal cluster models, with the exception of Fe$_2$O$_3$. 
4 Results and discussion

Table 13. Obtained reaction energy barriers with zero point energy correction ($E_a^{ZPE}$), molecular adsorption energy of H$_2$O$_2$ ($\Delta E_{ads}(H_2O_2)$); reaction energy ($\Delta E_r$) for the decomposition of H$_2$O$_2$ on the surfaces of some of the clusters shown in Figure 43 and the BEP coefficient obtained from Equation (8) ($\alpha_{BEP}$). The transition-state structures are shown in Figure 45, Figure 35d-Figure 37d. Energy values are in kJ·mol$^{-1}$.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>$\Delta E_{ads}(H_2O_2)$</th>
<th>$E_a^{ZPE}$</th>
<th>$\Delta E_r$</th>
<th>$\alpha_{BEP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>-88</td>
<td>60</td>
<td>-435</td>
<td>0.68</td>
</tr>
<tr>
<td>CuO</td>
<td>-62</td>
<td>71</td>
<td>-358</td>
<td>1.15</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>-150</td>
<td>11</td>
<td>-320</td>
<td>0.07</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>-54</td>
<td>56</td>
<td>-573</td>
<td>1.22</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>-66</td>
<td>36</td>
<td>-153</td>
<td>0.55</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>-150</td>
<td>42</td>
<td>-634</td>
<td>0.28</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-68</td>
<td>41</td>
<td>-490</td>
<td>0.60</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>-92</td>
<td>45</td>
<td>-684</td>
<td>0.49</td>
</tr>
</tbody>
</table>

From the BEP coefficients shown in Table 13, it is clear that the transition-states for the cleavage of H$_2$O$_2$ vary considerably in terms of the BEP classification methodology. For some of the oxides the decomposition of H$_2$O$_2$ is more structure sensitive than for others. The decomposition on Fe$_2$O$_3$ is the more structure sensitive and in HfO$_2$ the less structure sensitive. Relaxing the transition-states obtained Figure 45 leads to the formation of the products shown in Figure 46. The corresponding reaction energies are shown in Table 13.
The primary stable products of H$_2$O$_2$ decomposition consist of both adsorbed HO radical and H$_2$O. These interact with the clusters by forming bonded states with the metal cations, via the unpaired electron of HO$^*$ and the available non-bonding electrons more localized on the O atom in H$_2$O. For all cases, the formation of H$_2$O is due to the abstraction of a structural H atom by the HO$^*$ resultant of the cleavage of the O-O bond in H$_2$O$_2$ – the H atom is initially bound to an O atom of the cluster. The only cases where the primary product formed consists of 2 adsorbed HO radicals are Fe$_2$O$_3$ and HfO$_2$. This is interesting since the obtained transition state for H$_2$O$_2$ decomposition on Fe$_2$O$_3$ is with regard to an H atom transfer from H$_2$O$_2$ to a surface HO group which would indicate that water could be the primary product. Though, relaxing this geometry leads to a rearrangement of the structure and the spontaneous formation of 2 HO$^*$ bound to the two cations. This suggests that the H atom transfer mechanism might have a role in the decomposition of H$_2$O$_2$. Even if that role is minor when compared to the main reaction pathway which does not involve this process. This evidence is in agreement with the experimental finds reported in Section 4.5 and with the suggested mechanism for H$_2$ formation according to Reaction (R20). This is triggered by the removal of HO$^*$ from the system where H$_2$O$_2$ undergoes decomposition. In the experimental study for H$_2$O$_2$ reactivity presented in Sections 4.1.2.2 and 4.2.3 for a series of metal oxides, it can be seen that Fe$_2$O$_3$ behaves differently from the other oxides in terms of kinetic parameters and HO$^*$ formation dynamics. The contribution of the Fenton reaction for the
measured experimental energy barrier has to be considered. This would mean that the experimental data for Fe$_2$O$_3$ can have a contribution from a redox process. This could explain the discrepancy with the DFT obtained activation energy shown in Table 13.

### 4.6.2 $\chi$, IP, EA, and $\Delta E_{ads}$ (2HO$^\cdot$) as reactivity descriptors for the decomposition of H$_2$O$_2$ catalyzed by transition metal, lanthanide and aluminum oxides

In this section, the applicability of reactivity descriptors to the reaction of decomposition of H$_2$O$_2$ catalyzed by the oxides: ZrO$_2$, TiO$_2$, PdO$_2$, NiO$_2$, HfO$_2$, Fe$_2$O$_3$, Y$_2$O$_3$, Al$_2$O$_3$, Gd$_2$O$_3$, CeO$_2$ and CuO; is discussed. Whenever possible are derived reactivity descriptors whose parameters are values extracted from the experimental and DFT calculations presented in this thesis. Also, literature data is used for the derivation of some descriptors involving the Pauling electronegativity of the metal atoms present in the oxides.

One correlation that was briefly discussed in Section 4.4 is how the ionization potential of the metal cation present in the oxide influences the adsorption energy of the HO radicals. This was discussed based on the fact that upon adsorption of the HO radical, some of the electron density initially localized on the orbitals of the surface exposed metal atom, has to be delocalized in order to form bonded states with the unpaired electron of the HO radical. This causes the partial oxidation of the metal atoms that bind to the HO$^\cdot$. A correlation between the adsorption energy of HO$^\cdot$ and the ionization potentials of Zr$^{4+}$, Ti$^{4+}$ and Y$^{3+}$ was found. Following this, here is presented and discussed how the changes in the Mulliken charge of the metal cation present in the oxide correlate with the adsorption energy of the HO radicals for the various oxides. The adsorption energies of 2 HO radicals are for the binding of the radicals onto the hydroxylated clusters shown in Figure 43. The resulting plot showing the adsorption energies of the HO radicals as a function of the change in Mulliken charge ($e$) of the cations of the clusters are shown in Figure 47. The values for the change in Mulliken charges ($e$) were obtained as $e = M_p - M_r$. Where $M_p$ is the Mulliken charge of the cations in the product, and $M_r$ is the Mulliken charge of the cations in the reactant.
4 Results and discussion

Figure 47. Adsorption energy ($\Delta E_{ads}$ (2HO•)) of 2HO radicals as a function of the change in Mulliken charge of the metal cations accommodating the HO radicals ($e$). The value of $e$ is an average of the individual $e$ of the cations involved in the bonding with the 2HO•.

It can be seen (Figure 47) that there is a fairly linear correlation between the adsorption energies of HO radicals and the values of $e$. From this correlation it can be concluded that upon formation of bonds with HO•, the easier it is to delocalize electron density from the exposed orbitals of metal cation, the stronger the bonds with HO• will be. The strength of these bonds might have implications on the mechanism of decomposition of H₂O₂ because for the cases where the adsorption of HO• is stronger than a given threshold, surface poisoning by HO• might affect the overall reaction mechanism. On the other hand for the cases where the bonds of HO• with the surface are weaker, the HO• will probably be able to react further with H₂O₂ to form H₂O and HO₂•. The main outlier in the trend is Al₂O₃. This can be due to the fact that Al does not have $d$-orbitals or $f$-orbitals constituting its valence shell. The more “adsorbate readily available” shape of the 2$p$ orbitals accommodating the valence electrons of Al³⁺ might explain why a smaller change in $e$ for this cation, leads to a stronger $\Delta E_{ads}$ for HO•.¹⁸⁹

A measure of the tendency of an atom to attract electrons towards itself, is the Pauling electronegativity $\chi_P$.²⁰⁹ A plot of the $\Delta E_{ads}$ of 2 HO• as a function of $\chi_P$ of the atom accommodating the HO• is shown in Figure 48.
Figure 48. Adsorption energy of 2 HO radicals ($\Delta E_{ads}(2\text{HO}^*)$) obtained with DFT calculations using as reactants, the clusters of the transition metals shown in Figure 43, as a function of the Pauling electronegativity of the transition metal atom present in the oxide ($\chi_P$). $\chi_P$ are experimental data retrieved from literature.\textsuperscript{210}

For the data in Figure 48, the correlation coefficient between the Pauling electronegativity of the metal atom (in oxidation state 0) and the adsorption energy of the HO$^*$ is 0.92. This correlation holds only for the transition metal oxides studied. This can be explained with the following basis: The Pauling electronegativity is determined for the element in oxidation state 0. The removal of electrons to form the cationic species found in the oxides will cause relaxation of the electrons of the cation to minimize the energy of the new electron configuration. This relaxation will be different depending on the type of orbitals occupied in the different cations. Thus is expected that the more different the occupied orbitals are, the more different is the relaxation contribution that influences the shape and energy of the final relaxed orbitals after formation of the cationic species. From Figure 48:

$$\Delta E_{ads}(2\text{HO}^*) \approx (796 \times \chi_P - 2036).$$

The experimental data for the Arrhenius activation energies for decomposition of H$_2$O$_2$ on the surfaces of the oxides as well as the DFT data are shown in Table 14.
Table 14. Experimental Arrhenius activation energies ($E_a$); DFT electronic activation energies with zero-point-energy-corrections ($E_{aZPE}$) for decomposition of H$_2$O$_2$ on the surface of different oxides; and adsorption energies of 2 HO radicals onto hydroxylated clusters of the oxides $\Delta E_{ads}$ (HO). All values in kJ·mol$^{-1}$.

<table>
<thead>
<tr>
<th>Material</th>
<th>Experimental $E_a$</th>
<th>DFT $E_{aZPE}$</th>
<th>$\Delta E_{ads}$ (HO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>33 ± 1</td>
<td>42</td>
<td>-1028</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>37 ± 1</td>
<td>41</td>
<td>-778</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>44 ± 5</td>
<td>45</td>
<td>-1087</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>51 ± 1</td>
<td>11</td>
<td>-824</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>40 ± 1</td>
<td>60</td>
<td>-642</td>
</tr>
<tr>
<td>CuO</td>
<td>76 ± 1</td>
<td>71</td>
<td>-427</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>60 ± 1</td>
<td>56</td>
<td>-572</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>38$^a$</td>
<td>36</td>
<td>-1025</td>
</tr>
<tr>
<td>NiO$_2$</td>
<td>–</td>
<td>–</td>
<td>-404</td>
</tr>
<tr>
<td>PdO$_2$</td>
<td>–</td>
<td>–</td>
<td>-404</td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>63 ± 1</td>
<td>–</td>
<td>-540</td>
</tr>
</tbody>
</table>

a) Ref.$^{129}$

The DFT obtained energy barriers for H$_2$O$_2$ decomposition are in reasonable good agreement with the available experimental data (Table 14). The larger deviation found for CeO$_2$ and the fact that it was not possible to locate a transition-state for H$_2$O$_2$ decomposition on the Gd$_2$O$_3$ cluster show the limitations of the DFT methodology in describing the chemistry of lanthanides, especially that of Gd.$^{211,212}$ The transition-states for decomposition of H$_2$O$_2$ are a challenging system from a computational chemistry perspective. They consist of semi-radical states which are usually difficult to reproduce with DFT.$^{213}$ The transition-state for CeO$_2$ was found and the reaction energy barrier lays 20 kJ·mol$^{-1}$ above the experimentally determined value.

Following the concept by BEP, a plot of the adsorption energy of the HO radicals as a function of the experimental Arrhenius activation energy barriers was done. As discussed in Section 4.3.3, the adsorption of the HO radical contributes the most to the overall reaction energy when compared with the contribution from the molecular adsorption of H$_2$O.
4 Results and discussion

![Graph](image-url)

**Figure 49.** Experimental Arrhenius activation energies for H\textsubscript{2}O\textsubscript{2} decomposition ($E_a$) as a function of the adsorption energies of 2HO radicals ($\Delta E_{ads}$ (2HO•)) obtained with DFT calculations using minimal cluster models of the oxides (Figure 43). Data from Table 14.

It is visible (Figure 49) that, following the BEP principle, the more exothermic is the adsorption of the HO radicals, the lower is the activation energy barrier for H\textsubscript{2}O\textsubscript{2} decomposition. Worth of a remark is the fact that the experimental energy barriers were determined in solution. The cluster models consist of minimal sized clusters of stoichiometric units of the metal oxides whose terminations were truncated with H atoms and further hydroxylated. As the DFT data is for gas phase and given the good agreement with experiments, it seems plausible that the solvation effects have a small contribution for the energy of the reactions of adsorbed species during H\textsubscript{2}O\textsubscript{2} decomposition in the real systems. Nevertheless the extent and stability of the surface hydroxylation have an impact on the activation energy barriers for H\textsubscript{2}O\textsubscript{2} decomposition as it will be shown. In order to verify how the local properties of the surface atoms correlate with the experimental activation energies for H\textsubscript{2}O\textsubscript{2} decomposition, the experimental data was plotted as a function of the DFT values for IP and Mulliken electronegativities ($\chi$) of the cations present in the oxides (Figure 50 and Figure 51).
Figure 50. Experimental Arrhenius activation energies ($E_a$) as a function of the ionization potential of the cation present in the metal oxide.

The IP values (Figure 50) are the HOMO energies of the cations in the oxidation states present in the oxides in gas phase. In a similar way, for the determination of $\chi$ (Figure 51), the EA values used are the LUMO energies of the cations, in the oxidation states found in the oxides, in gas phase.

Figure 51. Experimental Arrhenius activation energies ($E_a$) as a function of the DFT obtained Mulliken electronegativities ($\chi$) of the cations present in the metal oxide.

The trend visible in Figure 50 does not follow a direct BEP relation in the sense that a lower IP of the cation means that the adsorption of HO radical product is more exothermic and as such the energy barrier for the reaction would be lower with decreasing IP. This simple correlation – depending only on the parameter: product adsorption energy – would be true for a reaction occurring on a dry surface (e.g. in UHV conditions). It has been discussed previously in this work and in a literature publication that the IP of a metal cation in a metal oxide surface is proportional to the Lewis acidity of the cation present in the oxide.\textsuperscript{214,215} As shown in Section 4.3.3, the more Lewis
5 Conclusions and summary.

acidic is the cation, the stronger it will bind the HO\(^{-}\) groups resulting from dissociative adsorption of H\(_2\)O. The effect of this on the mechanism of decomposition of H\(_2\)O\(_2\) is that this will lead to more extensive surface reconstruction and make the reactive surface site less available for accommodating H\(_2\)O\(_2\) and its decomposition products, ultimately leading to an increase in the energy barrier for H\(_2\)O\(_2\) decomposition at those cations which are more Lewis acidic. This trend is visible in the plot of Figure 50. Also, these different hydroxylation effects will, for the different materials, lead to different contributions – i.e. from geometric and electronic effects – to the BEP relation which causes its deviation from linearity.\(^{50}\) The more extensive the reconstruction of the hydroxylated site, the larger the contribution of a geometric effect to the BEP relation, and vice-versa.

The good correlation between reaction and catalyst properties obtained at a localized level – i.e. \(\Delta E_{ads}\) (2HO\(^{-}\)), IP and \(\chi\) – and the experimental data, indicates that the reaction of H\(_2\)O\(_2\) in the real particle systems is determined by local phenomena which is dependent on properties of the cations present in the oxides. This relation is shown here to be valid for a series of 8 oxides, 2 of which are lanthanides. The outlier is HfO\(_2\). This can be explained with the fact that even though hybrid DFT shows good performance for determining the HOMO/LUMO energies even for lanthanides,\(^{216}\) Hf is a special case in the sense that relativistic effects have to be considered, but the quasirelativistic ECP scheme applied here to Hf, implemented by Cundari and Stevens was parameterized for lanthanides with oxidation states 2+ and 3+.\(^{78}\) This fact contributes to the deviation in HOMO/LUMO energies prediction for Hf\(^{4+}\).\(^{217}\)

Even though the cluster models are fairly simplistic representations of the surfaces because they represent only a specific type of coordination site – with the exception of CeO\(_2\) and Fe\(_2\)O\(_3\) – the average absolute deviation from the experimental energy barriers (Table 13) is 4 kJ.mol\(^{-1}\). The origin of the discrepancy for CeO\(_2\) can be attributed to the limitations of the KS based DFT in modeling lanthanide reactivity. It is plausible that for Fe\(_2\)O\(_3\), the transition-state predicted with DFT does not correspond to the process determining the energy barrier in the real system.

5. Conclusions and summary.

From the experimental studies of the reactions of H\(_2\)O\(_2\) with a series of oxides it is possible to conclude that:

- For the same surface to volume ratio of oxide and the same concentration of reactant H\(_2\)O\(_2\), the reaction rate laws and rate constants differ widely between the different materials. Also the
heterogeneous rate constants – i.e. second order rate constants – are far from diffusion controlled.

- The reactions Arrhenius and enthalpy barriers differ widely for the different materials. The same is observed with the Arrhenius pre-exponential factors.

- The dynamics of formation of HO\(^\bullet\) during decomposition of H\(_2\)O\(_2\) are in agreement with the fact that HO\(^\bullet\) is a primary product of H\(_2\)O\(_2\) decomposition. Though, the yield of observed product of the scavenging of HO differs widely between the materials for the same consumption of H\(_2\)O\(_2\). This indicates that the relative reactivity of adsorbed species is different for the different materials.

- The formation of HO\(^\bullet\) was also observed for decomposition of H\(_2\)O\(_2\) on the surface of UO\(_2\) based materials. The mechanistic study indicates that the underlying factor for the differences between UO\(_2\) and SIMFUEL towards reaction with H\(_2\)O\(_2\), are differences in the redox reactivity of these materials.

The method for determination of HO\(^\bullet\) (implemented with basis in two previously published methods) reveals an effective strategy to observe the dynamics of formation of HO\(^\bullet\). This method is quite insensitive to interferences caused by the presence of the oxide. Though, a more in-depth study of the reactivity of the HO\(^\bullet\) scavengers Tris and TAPS has to be done in order to determine the effect of the surfaces on the selectivity of the reactions of surface/interfacial HO radicals with the scavengers.

The DFT models implemented for the DFT study are a computationally cheap and effective way of studying the reactivity of H\(_2\)O\(_2\) with the particles of the oxides. The density functionals that have shown an overall best performance are the M06 and PBE0. The average absolute deviations from experiments obtained with these functionals are 6 and 5 kJ\(\cdot\)mol\(^{-1}\) respectively for the energy barriers of the reactions of H\(_2\)O\(_2\) with ZrO\(_2\), TiO\(_2\) and Y\(_2\)O\(_3\).

In the study of the reactivity descriptors obtained from DFT, using the PBE0 functional, the minimal sized clusters were able to reproduce, the experimental data with an average absolute deviation of 4 kJ\(\cdot\)mol\(^{-1}\). This is for a set of 8 oxides. By plotting the experimental data against DFT obtained reactivity descriptors, good correlations which agree with the well-established Brønsted-Evans-Polanyi principle were found. Overall it can be concluded that:

- The adsorption of HO radicals causes delocalization of electron density of the metal cation accommodating those radicals. The more delocalization occurs, the more exothermic is the adsorption of HO\(^\bullet\) onto those surface atoms.
- The trend for adsorption energy of HO radicals is inversely proportional to the Pauling electronegativity of the metal atom present in the oxide. This trend was found for transition metal oxides.

- There is a correlation between the adsorption energies of the HO radicals and the energy barrier for H₂O₂ decomposition. The stronger the adsorption of product HO, the lower is the energy barrier for H₂O₂ decomposition, following the BEP principle.

- Both the DFT ionization potential and the Mulliken electronegativity of the bare metal cation (in the same oxidation state as it is present in the oxide) are inversely proportional to the energy barrier for H₂O₂ decomposition. This because the ionization potential is related with Lewis acidity of the cation which in turn determines the extent of its hydroxylation. The Mulliken electronegativity is related with the ease of delocalizing electron density from the metal cation.

All the reactivity descriptors obtained with DFT were calculated using minimal sized clusters consisting of one or two stoichiometric units of the oxides. These clusters represent defective surface sites in which the metal cations are undercoordinated. Given the very good correlations between computational and experimental data, it can be stated that for real oxide materials, the processes that account for the pathway and energetics of the decomposition of H₂O₂ are very localized (i.e. at the atomic scale) and are highly dependent on the local properties of the cations present in the oxides. This also indicates that the surface defects where the metal cations are more undercoordinated have an important role in determining the reaction kinetic and energetic parameters on the real systems.

6. The contribution of this work to the field of interfacial radiation chemistry

A method was implemented for the detection of HO radicals in solution and interfaces. This is a simple method that can be performed easily in for example, a basic chemistry lab. This method can be applied to many systems such as the study of reactor chemistry, photocatalysis, heterogeneous catalysis, etc. A computationally efficient methodology was developed for the study of the reactions of radiolysis products of water and different metal oxide surfaces. This has brought understanding of the mechanisms of interaction and reactivity of H₂O₂ and HO radical with surfaces. It is demonstrated that the HO radicals formed in solution can be trapped by surfaces. This also raises new questions about the significance of this process in the corrosion of nuclear reactor components. The important role of the interactions of the HO radical with these surfaces is further illustrated by the spontaneous production of H₂ when HO• scavengers are present in the
system where H\textsubscript{2}O\textsubscript{2} undergoes decomposition. Future studies on the interactions of HO\textsuperscript{•} – and eventually other radicals – with surfaces are necessary. This in order to clearly elucidate the importance of this species in the formation of H\textsubscript{2} at oxide and metallic surfaces and its role in corrosion processes.

Together, the experimental and computational studies lead to surprising results such as the fact that the complex chemistry of H\textsubscript{2}O\textsubscript{2} reacting with solid surfaces in liquid phase can actually be described to a good extent by using fairly simple theoretical models of the metal oxides surfaces.

This study lead to the identification of the properties of the oxides surfaces that account for their reactivity towards some radiolysis products. This knowledge, together with the kinetic, energetic and mechanistic data obtained here can be used as a predictive tool for analyzing reactor chemistry and can aid in the design of improved new functional materials to be used within nuclear technology.

7. Supplementary Information: Density Functional Theory

To completely describe the spatial coordinates of an atom, it is necessary to define both where its nucleus is and where the atom’s electrons are. The early definition of the atom, much inspired by the planetary motion, considered the atom as being a number of electrons e orbiting a nucleus with charge Ze. From a classical mechanics point of view, defining the spatial coordinates of the atom sounded like a regular many-body problem that could be tackled by using Newton’s equations of motion. However, experimental observations were incompatible with this view of the orbiting electrons around a nucleus resembling the solar system. According to the predictions of electromagnetic theory, the electrons in orbital motion, due to the radial acceleration would decelerate and collapse into the nucleus. This would mean that matter would be unstable, clearly an observation far from reality. From the attempts to study the atom and its constituents, Niels Bohr reached a very important conclusion that postulated that the orbits that the electrons occupy have specific energies and spatial radii. In order for the electrons to “jump” in between different orbits, it would be necessary that they absorb or release a quantum of energy. The whole set of ideas that surrounded this discovery together with Planck’s observations of the blackbody radiation ultimately led to the development of the mathematical tools that became the quantum theory of matter or quantum mechanics.

The energy of a system of quantum bodies is expressed according to the time-independent form of the Schrödinger equation
where $H$ is the Hamiltonian operator and $\Psi$ is a set of solutions, or eigenstates, of the Hamiltonian. Each of the solutions $\Psi_n$ of the set $\Psi$, has an associated eigenvalue, $E_n$, that satisfies the eigenvalue equation. This equation means that for a system of quantum bodies, there is a wavefunction $\Psi$ over which an operator can be applied and all the properties of the system can be derived by solving the time-independent Schrödinger equation. When applied to electrons, as these particles are fermions, the total electronic wave function must be antisymmetric i.e. it must change sign; whenever the coordinates of two electrons are exchanged. This is known as exchange. If one is interested in obtaining the energy of the system, the operator to apply to the wavefunction is the Hamiltonian operator as stated in Equation (17). The detailed definition of the Hamiltonian depends on the physical system being described by the Schrödinger equation. There are several well-known examples like the particle in a box or the harmonic oscillator where the Hamiltonian has a simple form and the Schrödinger equation can be solved exactly. Though, when applied to the movement of electrons in an atom, the multi-component many-body problem posed by the Schrödinger equation is unsolvable in an exact way for a system more complex than hydrogenoid atoms or the He$_{2}^{+}$ molecule. For more complex systems, the fact that those are many-body systems, plus the existence of Coulomb interactions makes the Schrödinger equation not separable. For describing an atom with $Z$ electrons, it is possible to tackle the multielectronic problem as a product of antisymmetrical one-electron wavefunctions (a Slater determinant). The Hartree-Fock (HF) method assumes that the exact, $N$-body wave function of a system of fermions can be approximated by a single Slater determinant.$^{218}$ This approach however, assumes separability of the Schrödinger equation, implying that the probability of finding an electron at a point in space is essentially independent of the location of the other electrons. This picture does not account for the repulsive electron-electron interactions because an electron located at a region of space $r$ will create an “exclusion zone” where other electrons will not be found (Figure 52). The HF method is computationally cheap but the fact that it neglects correlation produces data with large deviations from experimental results.$^{219}$
Figure 52. Exclusion zones leading to correlation holes (waving lines) for a system of 3 electrons (●). The arrows represent two particle correlation. It is possible to conceptually express the total correlation \( X \) of this system as: \( X_{\text{Total}} = ij + jk + ik \).

Thus, the probability of finding our electron at the point of space \( r \) will depend of its interactions with the other \( Z-1 \) electrons that constitute the atom – and these interactions depend on the spatial coordinates of the \( Z-1 \) electrons. This phenomenon is known as correlation. It implies that the many-body wave function must contain terms that depend on two electron coordinates (Figure 52). As such, the approach of the total wave function in terms of one electron wavefunctions is in many cases rough. For a system of \( M \) nuclei and \( N \) electrons all this means that the Schrödinger equation cannot easily be decoupled into a set of simpler equations, which implies that to solve the Schrödinger equation we have to deal with \( 3(M+N) \) coupled degrees of freedom.

An underlying principle for applying quantum mechanics to atoms resides in the fact that atomic nuclei are much heavier than individual electrons. From a classical mechanics perspective, when this principle is applied to the movement of electrons and nuclei, it means that electrons respond much more rapidly to changes in their surroundings than nuclei do. As a result, under the conditions of applicability of this approximation, it is possible to split the position problem into two parts. First, for fixed positions of the atomic nuclei, we solve the equations that describe the motion of the electrons. It means that for a given set of electrons moving in the field of a set of nuclei, we find the lowest energy configuration, or state, of the electrons. The lowest energy state is known as the ground state of the electrons, and the separation of the nuclei and electrons into distinct mathematical problems is the Born-Oppenheimer approximation. For \( M \) nuclei with positions \( R_1, \ldots, R_M \), it is possible to express the ground-state energy, \( E \), as a function of the positions of these nuclei, \( E(R_1, \ldots, R_M) \). This
function is the adiabatic potential energy surface of the atoms. And this approximation is known as the adiabatic approximation. Once it is possible to calculate this potential energy surface, it is possible to solve the problem: how does the energy of a material change as we move its atoms in space?

Since the development of the quantum mechanical formulations of matter, there has been a diversity of approaches for approximating a solution to the Schrödinger equation for many-electron systems. One of the most successful approaches is the one developed after two mathematical theorems that were demonstrated by Kohn and Hohenberg, and the further derivation of a set of equations by Kohn and Sham. The Kohn-Hohenberg approach provides an elegant way to approximate electron correlation with resource efficiency similar to that of Hartree-Fock. The first theorem by Kohn and Hohenberg states that: The ground state energy obtained from the Schrödinger equation is a unique functional of the electron density. This means that for an electron system, there is a relation between the ground state wave function and the ground state electron density. This relation is measured by a functional of the electron density. When applied to the energy of a system, the Hohenberg and Kohn’s theorem says that the ground state energy $E$ can be expressed as $E[n(r)]$ where $n(r)$ is the density of $n$ electrons at the spatial coordinates $r$. This is the origin of the term density functional theory (DFT). It implies that the ground state electron density uniquely determines all properties of the system, including the energy and wave function, of the ground state.

DFT marked an enormous progress in the understanding of quantum systems. As an example: "Why is this result important? It means that we can think about “solving the Schrödinger equation” by finding a function of three spatial variables, the electron density, rather than a function of $3N$ variables, the wave function. Here, by “solving the Schrödinger equation” we mean, to say it more precisely, finding the ground-state energy. So for a nanocluster of 100 Pd atoms the theorem reduces the problem from something with more than 23000 dimensions to a problem with just 3 dimensions."

Although the form of the functional that provides an exact solution for the electronic Schrödinger equation is not known, the second theorem by Hohenberg-Kohn defines a property of the functional that allows its practical application to multi-electronic problems: The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation. This turns the problem of finding the approximate true electron density, onto a variational problem. A variational principle is used with approximate forms of the functional to determine solutions that satisfy the principles underlying the Schrödinger equation. Over the years, several functional forms have been
developed with the intent of approximating the many-body problem posed by the Schrödinger equation, from the electron density perspective. The simpler case of applicability of the true functional of the electron density – whose existence is shown by the Hohenberg-Kohn theorem but whose form is unknown – is the case where this functional can be derived exactly. This is possible for the uniform electron gas. For a uniform electron gas the density is constant in all points of space. The practical applicability of this approach is somehow limited because chemical properties and chemical bonds are the result of variations in electron density in a molecule or material. Nevertheless for such uniform electron gas, the Kohn-Sham (KS) equations can be applied in a practical way. The concept behind the applicability of the KS equations builds in the fact that the exchange-correlation potential can be set at each position of space to be the known exchange-correlation potential obtained from the uniform electron gas for the electron density observed in that point of space. Because this method uses only the local density to define an approximation of the exchange-correlation functional, it is known as the local density approximation (LDA). The LDA is a tool to define the KS equations but its results are not the exact solution of the Schrödinger equation. This is because the LDA approach is not leading to the true form of the exchange-correlation functional. Recall that the true form of the exchange-correlation functional was demonstrated by Hohenberg-Kohn to provide an exact solution to the Schrödinger equation but from the electron density perspective instead of from a wave-function perspective. The problem of finding accurate approximations to the exact exchange-correlation functional is the biggest challenge of Kohn-Sham DFT. The better we understand the exact functional, the better approximations we can design.

At this point, our intuition as chemists tells us that the LDA functional form as it is presented above should not provide the best description of the physical properties of electron systems, which, are behind chemical properties of molecules and materials. These are: changes in electron density, electronic correlation, spin density gradients, spin-up/spin-down kinetic energy dependence, spin polarizabilities etc. Since the introduction of the LDA concept, there has been published a multitude of different approaches and improvements to the functional forms in order to better describe the chemistry of real systems.

The generalization of LDA that includes electron spin is called local spin density approximation (LSDA). The energy obtained from LSDA calculations will at each spatial coordinate depend on electron spin i.e. $\alpha(\uparrow)$ or $\beta(\downarrow)$. The next approximation after the LDA and LSDA was the development of a class of functionals that uses information of both the local electron density and the local gradient of the electron density. This is the generalized gradient approximation (GGA). In spite of being also a local
approximation, the inclusion of a gradient dependency of the energy in the
GGA lead to improved results when compared with the LSDA approaches for
calculations of: total energies,\textsuperscript{227} atomization energies,\textsuperscript{227,228} energy barriers
and structural energy differences.\textsuperscript{229-231} One can think directly that the GGA’s,
because it incorporates more physical information, always performs better
than the LDA based approaches. This is not always the case and for example
GGA calculations soften chemical bonds, an effect that sometimes corrects\textsuperscript{231}
and sometimes overcorrects\textsuperscript{232} the LSDA predictions. Typically, GGA’s favor
density inhomogeneity more than LSDA does. Overall the GGA for the
exchange-correlation energy are an improvement over the LSDA description
of atoms, molecules, and solids. Because there are many ways in which to
include the shape of the gradient of the electron density on the functional,\textsuperscript{54}
there is a large number of types of GGA functionals. Two of the most widely
used functionals in calculations involving solids are the Perdew–Wang
functional (PW91)\textsuperscript{53} and the Perdew–Burke–Ernzerhof functional (PBE).\textsuperscript{54} The
PBE is a parameter free functional which was constructed by making the
functional form to satisfaction some constrains. Further developments after
the GGA have been developed and lead to more and more sophisticated
classes of functionals which use other pieces of physical information. In fact
it is claimed that a hierarchy of functionals can be constructed that gradually
include more and more detailed physical information. Because of the
different type of information that many of the functionals include, it is
difficult to state which are “more correct”. According to a recent review,\textsuperscript{233}
six strategies have been widely employed for designing density functionals:
(1) local spin density approximation (LSDA), (2) density-gradient expansion,
(3) constraint satisfaction, (4) modeling the exchange-correlation hole, (5)
empirical fits, and (6) mixing Hartree–Fock and approximate DFT exchange.
Other more sophisticated functionals appeared after the GGA’s. The meta-
GGA’s (MGGA) are the next step in functional improvement as they go
beyond the gradient correction. This class of functionals takes into account
the second derivative of the density, i.e, the Laplacian. Becke and Roussel
were the first to proposed an exchange functional (BR) having such
dependence.\textsuperscript{56} Numerically stable calculations of the Laplacian of the density
pose something of a technical challenge, and the somewhat improved
performance of MGGA functionals over GGA analogs is balanced by this
slight drawback. An alternative MGGA formalism that is more numerically
stable is to include in the exchange-correlation potential a dependence on the
kinetic-energy density $\tau$. The BR functional includes dependence on $\tau$ in
addition to its already noted dependence on the Laplacian of the density.
Other developers, however, have tended to discard the Laplacian in their
MGGA functionals, retaining only a dependence on $\tau$. Various such MGGA
functionals for exchange, correlation, or both have been developed including
B95, B98, ISM, KCIS, PKZB, HCTH, TPSS, and VSXC. The cost of an MGGA calculation is entirely comparable to that for a GGA calculation, and the former is typically more accurate than the latter for a pure density functional.

Observations that the LDA and GGA trends deviated from the HF results led to the development of a new concept in the implementation of functionals – the inclusion of HF exchange. These functionals involve a DFT correlation with a combination of DFT and HF exchange. This class of functionals is designated by hybrid functionals and their implementation is based on

\[ E_{XC}^{hyb} = \alpha E_X^{HF} + (1 - \alpha) E_X^{DFT} \]

where \( E_{XC}^{hyb} \) is the exchange-correlation energy of the hybrid functional, \( \alpha E_X^{HF} \) is the HF exchange energy, \( E_X^{DFT} \) is the DFT exchange energy, \( E_C^{DFT} \) is the DFT correlation energy. \( \alpha \) is either chosen to assume a specific value – between 0 and 1 – or is obtained by fitting; in a way that the resulting functional performs the best in predicting the properties of a molecular database. One example of the later type of approach for the determination of the amount of HF exchange to include in the hybrid functional is the B3LYP functional. This functional was optimized to reproduce geometries and binding energies of molecular systems to the same accuracy of low-level quantum chemical methods with the advantage of a significantly lower computational cost. B3LYP can provide accurate molecular geometries even when hydrogen bonds are present.

The other approach, that consists in fixing \( \alpha \) a priori was behind the development of the PBE0 functional. This functional form was obtained by supplying the PBE GGA functional with a predefined amount of exact exchange. The PBE0 functional has shown very good performance for structural, thermodynamic, kinetic and spectroscopic (magnetic, infrared and electronic) properties. The way in which the functional is derived and the lack of empirical parameters fitted to specific properties make the PBE0 model a widely applicable method for both quantum chemistry and condensed matter physics. It has been reported improved performance of the PBE0 functional over the B3LYP for properties of systems containing light and heavy metals.

The latest class of functionals developed following the approaches above described are the hybrid-meta-GGA. This type of functionals combine the inclusion of HF exchange with the meta GGA approach. One such functional that has revealed improved performance over some meta and hybrid functionals is the M06 functional. This functional, besides of the Laplacian dependency of the density, includes a dependence on the electronic kinetic-energy density \( \tau \). This is up-spin down-spin dependent. This functional was also parameterized to be self-interaction error free (SIE). The SIE is a feature of DFT that results from the fact that the interaction of an electron with itself.
is accounted for in the exchange-correlation functionals obtained from the LDA, GGA and MGGA approximations. The hybrid functionals correct the SIE due to the inclusion of HF exchange. The SIE results from a physically unreasonable property that leads to poor performance of the functionals especially in describing systems with non-integer number of electrons. This means that the functionals which are not free from SIE have problems also in describing transition states of chemical reactions (especially those involving homolytic bond cleavage) and charge-transfer complexes. For solids and surfaces, it has been recently shown that hybrid DFT functionals that contain a certain amount of Hartree-Fock exchange are necessary to accurately describe the electronic states of nonmetallic solids and the defects in metal oxides. In order to properly describe the electronic properties of the defects of TiO$_2$ surfaces for example, it is necessary to recur to the usage of functionals that incorporate a certain amount of Hartree-Fock exchange. The pure DFT functionals, due to the self-interaction error, fail to give a localized character to trapped electron states and holes in TiO$_2$ surface defects. When unpaired electronic states are present in the system, this type of functionals will tend do delocalize the electron density in order to minimize the self-interaction error, thus giving results for electron density in surface defects that are poor when compared with experimental data. This situation has been evident whenever pure DFT functionals were used for describing defects in large band gap semiconductors and insulators. Other discrepancies were found in the type of minima for the bonding between HO$^+$ and H$_2$O when these systems were described with pure DFT functionals. Although these situations can be improved by using HF exchange in the functionals, the empirical formalisms to correct for the SIE did not lead to good performing functionals for systems where fractional charge behavior is present, polarizabilities of polymers and dissociation of molecules.

In order to solve the electronic structure problem, using HF, post-HF or DFT, it is required that we choose a mathematical representation of the one-electron orbitals. The basis set is the set of mathematical functions from which the electron density or wave function is constructed. In HF theory, each molecular orbital is expressed as a linear combination of basis functions for which the coefficients are determined in an iterative way by finding solutions to the HF self-consistent-field equations. As described above the HF wave function is constructed from individual occupied molecular orbitals. The HF limit is achieved by use of a hypothetical infinite basis set, which would permit the optimal description of the electron probability density within the HF approximation. The one-electron wave functions are expanded in a generic basis set described by a set of orbitals. The Kohn-Sham or Hartree-Fock orbitals are then written as a linear combination of these orbitals in a similar way to the Hückel method. It is thus important to
identify the mathematical functions that allow wave functions to approach the HF limit and at the same time being efficient. There has been a multitude of approaches for constructing basis set depending also on the application that the developers have in mind i.e. periodic or molecular systems etc. For molecular systems, the type used is atom-centered basis sets. Within this concept, the most common approach is to expand the one-electron wave functions (molecular orbitals) in terms of atomic orbitals which are centered in the atomic nuclei and are represented in terms of basis functions with different functional forms or can be given numerically on a grid. The tighter or denser this grid is, the easier it is to achieve convergence of the SCF cycle and the more precise is the calculation. A basis set should allow for improvement of its quality when the number of basis functions is incremented. If a single basis function per atomic orbital is used, the basis set is minimal or single-ζ (SZ). These basis sets can be accurate for isolated atoms but have limitations in describing molecular systems where electrons are involved in chemical bonding and the electron density becomes polarized. If one more set of basis functions per orbital is added it becomes a double-ζ (DZ) basis set. More accuracy and flexibility can be achieved by adding more basis functions of the same type, forming the triple-ζ (TZ) basis set. Given that the core states of an atom are rather insensitive to their environment, the usage of multiple basis functions for describing core states is not common. Generally the basis set splitting is applied to the valence orbitals forming the split valence basis sets. The basis sets can be further improved by accounting for polarization effects. These, account for the deformation of atomic orbitals due to the presence of neighboring atoms. Their description requires the introduction of functions of different angular momenta. The presence of polarization functions in a basis set is denoted by “*”. For negatively charged systems, the Coulomb repulsion between electrons leads to the spread of the atomic orbitals. To better represent these orbitals – which the standard basis functions are not able to represent – additional basis functions have to be included. These are usually functions with small exponents and are called diffuse functions and are indicated by a “+” sign. One “+” for one diffuse function, “++” for two, etc. These functions are useful for describing non-bonding interactions.

A very valuable observation in what concerns optimizing computational resources is that the core electrons in atoms are not involved actively in chemical bonding. As such they don’t need to be treated explicitly in terms of a set of orbitals with a corresponding set of functions. The core electrons can then be treated by of using a nodeless pseudo-wave function. This is not an orbital anymore but it is the lowest lying state of an effective pseudo-potential or effective core potential (ECP) which replaces the true potential. This principle is the basis of the design of the ECP basis sets. The number of
electrons treated explicitly is then much smaller and the number of required
electronic states and basis set size is reduced significantly. This approach is
particularly useful for the study of metals for which the explicit treatment of
the core electrons would make the calculations involving these elements
computationally prohibitive. Relativistic effects can also be incorporated in
ECP basis sets.\textsuperscript{77} This is particularly useful for calculations involving heavier
transition metals or lanthanide and actinide elements.\textsuperscript{78} The design of basis
sets based on the ECP approach has expanded to the point where ECP basis
sets have been developed for very specific applications such as calculations
of properties of specific clusters of certain elements.\textsuperscript{237} Tough, some authors
claim that such approach is incompatible with the \textit{ab initio} concept.
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