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PROGRAMA DE PÓS-GRADUAÇÃO EM MODELAGEM MATEMÁTICA E COMPUTACIONAL

COMPUTATIONAL STUDY ON THE CO₂ REDUCTION INTERMEDIATES OVER CU₅₅ NANOCLUSTERS DOPED WITH COBALT

GUILHERME VON RONDOW NASCIMENTO

Orientador: Breno Rodrigues Lamaghère Galvão
Centro Federal de Educação Tecnológica de Minas Gerais

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GUILHERME VON RONDOW NASCIMENTO

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DOPED WITH COBALT**

Dissertação apresentada ao Programa de Pós-graduação em Modelagem Matemática e Computacional do Centro Federal de Educação Tecnológica de Minas Gerais, como requisito para a obtenção do título de Mestre em Modelagem Matemática e Computacional.

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Orientador: Breno Rodrigues Lamaghère Galvão
Centro Federal de Educação Tecnológica de Minas Gerais

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***“COMPUTATIONAL STUDY ON THE CO₂ REDUCTION INTERMEDIATES
OVER CU₅₅ NANOCCLUSERS DOPED WITH COBALT”***

Dissertação de Mestrado apresentada por **Guilherme Von Rondow Nascimento**, em 15 de dezembro de 2022, ao Programa de Pós-Graduação em Modelagem Matemática e Computacional do CEFET-MG, e aprovada pela banca examinadora constituída pelos professores:

Prof. Dr. Breno Rodrigues Lamaghere Galvão
Centro Federal de Educação Tecnológica de Minas Gerais

Prof. Dr. Heitor Avelino de Abreu
Universidade Federal de Minas Gerais

Prof. Dr. Thiago Gomes de Mattos
Centro Federal de Educação Tecnológica de Minas Gerais

Visto e permitida a impressão,

Prof.ª Dr.ª Elizabeth Fialho Wanner
Presidenta do Colegiado do Programa de Pós-Graduação em
Modelagem Matemática e Computacional

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Resumo

Os principais problemas ambientais, como o efeito estufa, são decorrentes do avanço da industrialização e da exploração excessiva dos combustíveis fósseis. A queima destes combustíveis libera uma grande quantidade de CO_2 na atmosfera. Nesse contexto, a redução eletroquímica do CO_2 oferece a possibilidade de remover este poluente da atmosfera e transformá-lo em produtos químicos de forma sustentável. Assim, investigar os intermediários eletroquímicos da redução pode fornecer insights sobre os mecanismos para converter CO_2 eletroquimicamente. Neste trabalho, algumas etapas da redução eletroquímica do CO_2 é estudada usando a Teoria do Funcional Densidade (DFT), funcional PBE com correção D3 implementada no pacote de simulação Viena *ab initio* (VASP). Como primeiro passo, cálculos são realizados para determinar a estrutura de menor energia para um cluster de 55 átomos. Depois, um átomo de cobre foi substituído por um átomo de cobalto em diferentes posições possíveis. Para investigar as interações entre o adsorbato e os aglomerados, cálculos preliminares de triagem são realizados para fornecer uma prévia dos locais e possibilidades de adsorção. As configurações mais relevantes são posteriormente refinadas com cálculos de nível superior. Os resultados mostram que H, OH, CO e COH tendem a adsorver em sítios *hollow*, enquanto HCO tem preferência em sítios *bridge*. Quando o cluster é dopado em subsuperfície, os adsorbatos H e COH mantêm sua preferência por sítios *hollow*, o mesmo acontece com HCO, que se mantém em sítio *bridge*, enquanto OH e CO preferem adsorver em sítios de *bridge* e *top* respectivamente. Se o átomo dopante estiver presente na superfície do cluster, H, OH e COH adsorvem em sítios *hollow*, enquanto CO e HCO têm preferência em adsorver em sítios *top* e *bridge*, respectivamente. Cálculos empregando o modelo do eletrodo de hidrogênio foram realizados com os sistemas mais estáveis, a adsorção do CO é favorável, entretanto a formação do COH e HCO requerem mais energia, resultados mostram também que a dopagem apresenta maiores diferenças quando a mesma é feita na superfície do cluster.

Palavras-chave: estrutura eletrônica, DFT, nanoclusters, catálise.

Abstract

Major environmental problems, such as greenhouse, are arising from advances in industrialization and the excessive exploration of fossil fuels. The burning of these fuels releases a large amount of CO_2 in the atmosphere. In this context, the electrochemical reduction of CO_2 offers the possibility of removing this pollutant from the atmosphere and transforming it into chemical products in a sustainable way. Thus, investigating the electrochemical intermediates reduction may provide insights into the mechanistic pathways of converting CO_2 electrochemically. In this work, some steps of the electrochemical reduction CO_2 is studied using Density Functional Theory (DFT), PBE functional with D3 dispersion correction implemented in the Vienna *ab initio* simulation package (VASP). As a first step, calculations are made to determine the lowest energy structure for a cluster with 55 atoms. Afterwards, one atom of copper has been replaced by a cobalt atom in different possible positions. For investigating the interactions between the adsorbate and the clusters, preliminary screening calculations are performed to provide a first glimpse on the adsorption sites and possibilities. The most relevant configurations are later refined with higher level calculations. The results show that H, OH, CO and COH have a tendency to adsorb in hollow sites, while HCO has a preference for bridge ones. When the cluster is doped in the subsurface, the adsorbates H and COH maintain their preference for hollow sites, the same happens with HCO, which maintain in bridge site, while OH and CO prefer to adsorb in bridge and top sites respectively. If the dopant atom is present in the surface of the nanocluster, H, OH and COH adsorb in hollow sites, while CO and HCO have a preference to adsorb in top and bridge sites respectively. Calculations employing the computational hydrogen electrode model were performed with the most stable systems, the CO adsorption is favorable, however the COH and HCO formation require more energy. The results also show that doping presents greater differences when it is done on the surface of the cluster.

Keywords: electronic structure, DFT, nanoclusters, catalysis.

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Chapter 1

Introduction

The increase in CO₂ emissions in the atmosphere has led to major environmental problems, and the greenhouse effect is one of the main, since it affects sustainable social and economic development (LI et al., 2020). Through Figure 1 we can see the growth in the global CO₂ concentration. Estimates say that there was an increase approximately from 277 ppm in 1750 to 417.2 ppm in 2022, which represents an increase of 51% of CO₂ concentrations.

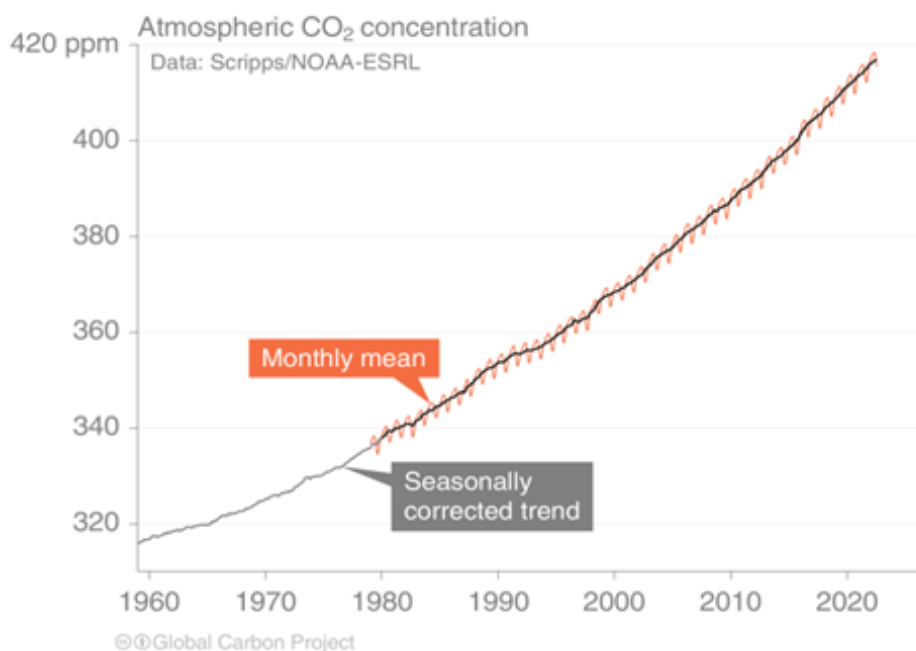


Figure 1 – Global CO₂ concentration in the atmosphere over the years.

Source: (FRIEDLINGSTEIN et al., 2022)

Figure 2 shows that the decrease in CO₂ emissions occurred in isolated events in the world, such as global financial crisis and COVID-19 pandemic but quickly increased again. Global

fossil CO₂ emissions have increased by around 63% when we compare the results of 1990 and 2021 and the countries that contribute most to these emissions are China and USA.

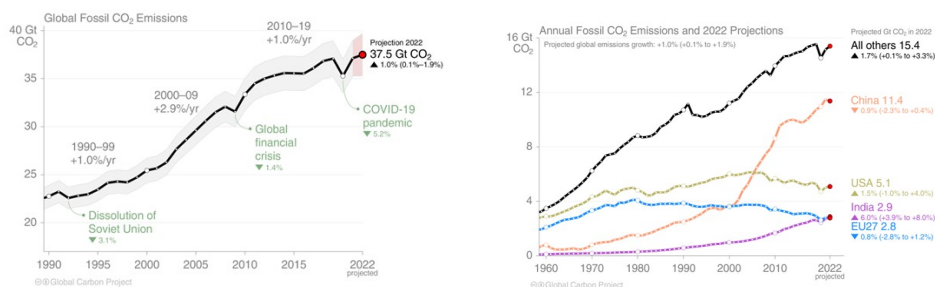


Figure 2 – Global CO₂ concentration in the atmosphere over the years and 2022 projections according to the emissions of each country.

Source: (FRIEDLINGSTEIN et al., 2022)

Therefore, given this scenario it is necessary to research in this area in order to reduce CO₂ emissions or utilize it in another way, for example, as a source of carbon for the chemical industry. In this sense, the removal of CO₂ from the atmosphere has attracted great interest and strategies of CO₂ storage and CO₂ reutilization have been proposed (LIU et al., 2021).

An alternative to mitigate the increase of CO₂ emissions, would be the electrochemical CO₂ reduction reaction, as it uses renewable energy to convert CO₂ into value-added products such as CO, ethylene, and other hydrocarbons or oxygenates. One of the advantages of using this process is high scalability, causing the CO₂ to be electrochemically reduced to valuable fuels and chemicals in a sustainable way (JOUNY; LUC; JIAO, 2018).

In chemistry, a cluster is an ensemble of bonded atoms intermediate in size between a molecule and a bulk solid. Transition metal clusters show growing technological importance in the fields of catalysis due to their unique properties, mostly the properties on the activation and adsorption of this molecule. Nanoclusters have been exploited as a new possibility since they are useful models for identifying the characteristics of catalytic sites to design new catalysts (MORATO-MÁRQUEZ et al., 2020).

Copper-based catalysts have attracted many studies, due to their ability to produce alcohols and hydrocarbons from CO₂ and also because their selectivity and activity vary with their structural properties. Comprehending the electrochemical CO₂ reduction reaction (CO₂RR) on copper surfaces can be useful to design new catalysts (VERGA et al., 2022). A perspective to improve the performance of copper catalysts would be doping them with other metals, since the mixture will affect the interaction of reactants, intermediates and products on the surface of the catalyst (BERNAL et al., 2018).

Doping can enhance the catalytic performance due to the change in the electronic structure when compared with monometallic systems (NABI et al., 2022). Thus, a mixture of copper and another metal will affect the interaction of reactants, intermediates, and products at the surface of the catalyst. It is expected then that this effect will adjust the desired structural, electronic, catalytic, and magnetic properties for potential applications in materials science, solid state chemistry, microelectronics, and nanotechnology (LING et al., 2015).

Other parameters can also change the activity and selectivity when the CO₂RR catalysts are nanoparticles (NP), such as their size for example. According to (BERNAL et al., 2018) the structure and surface composition of a bimetallic NP may differ from that of bulk, and exposure of the catalyst to certain environments, treatments or reaction conditions can lead to drastic changes that may also evolve in the course of the reaction.

The focus of this work is to study the intermediates of CO₂RR using the Cu₅₅ nanocluster and its singly cobalt doped variant (Cu₅₄Co) as catalysts. It will be studied the interactions among H, OH, CO, COH and HCO with the nanocluster. H and OH are always present in the reaction medium, and the other molecules are important intermediates of CO₂RR. We will also evaluate the effect of the cobalt over each intermediate to address if it can modify the reaction course.

The next chapters of this work will be divided as follows. Primarily, some theoretical concepts will be considered, such as what are nanoclusters and theory density functional (DFT) which are concepts important for the development of this dissertation. In the methodology chapter will be presented the computational details and how the calculations were performed. In the results chapter, there will be a presentation of analyses concerning the adsorption steps of the cluster non-doped and of the cluster doped with the CO₂RR intermediaries. In the conclusion, the last chapter, are the considerations about the results and also what is believed can be added for future papers.

Chapter 2

Theoretical Background

In this chapter, the theory that underpins the results obtained in this work will be presented. It is possible to apply to nanoclusters the same theoretical fundament that are applied to studying molecules, the quantum mechanical methods ranging from ab initio variational calculations of the entire electronic structure, to more approximate methods to describe the motions of the atoms, molecules or ions comprising the cluster ([HABERLAND, 1994](#)).

2.1 Clusters

According to [Johnston \(2002\)](#) the term cluster means an aggregate of a countable number ($2 \cdot 10^n$, where n can be as high as 6 or 7) of particles (i.e. atoms or molecules). The constituent particles may be identical, leading to homo-atomic (or homo-molecular) clusters, A_a , or they can be two or more different species - leading to hetero-atomic (hetero-molecular) clusters, $A_a B_b$. These clusters may be studied in the gas phase, in a molecular beam, adsorbed onto a surface or trapped in an inert matrix.

The importance in the study of clusters is given to the fact in which they constitute a new kind of material that can have diverse properties from those individual atoms and molecules or bulk matter. Both the geometric shape and the energetic stability of clusters may drastically change with size, and this is a reason for the interest in clusters. Due to the high applicability of these materials more research is being made, mostly in fields such as catalysis and nanoelectronics (e.g., in single-electron tunneling devices) ([FERRANDO; JELLINEK; JOHNSTON, 2008](#)).

2.1.1 Nanoalloys

According to [Johnston \(2002\)](#) metal clusters may be composed of a single metallic element or of more than one metal, giving rise to the subclass of intermetallic or (nanoalloy) clusters.

In materials science, the range of properties of metallic systems can be greatly extended by taking mixtures of elements to generate intermetallic compounds and alloys. In most cases, there is an improvement in the specific properties of the alloy due to synergy effects and the wide variety of compositions, structures and properties of the metal alloy, leading to a wide application in diverse fields of research, such as engineering and catalysts (FERRANDO; JELLINEK; JOHNSTON, 2008).

Nanoalloys, present a high degree of tunability due to their abundance of possible spatial arrangements (LAASONEN et al., 2013). Nanoalloys are specified by their geometric structure and by its chemical ordering. The growing interest is because of the fact that nanoalloys present magic size which benefit when modeling the chemical ordering and the structure of them, due to their enhanced structural, electronic, and thermodynamic stability. Sizes as 19, 23, 26, 38 e 55 are magic numbers for icosahedron structure and knowledge about these magic sizes have valuable information for technological applications (YILDIRIM; ARSLAN, 2022).

Clusters are constantly applied in catalysis, and understanding the reactivity of transition metals that make up the cluster is essential to model catalysts. The surface of metallic catalyst, in general affects the catalytic process, because it lowers the activation barrier to bond breaking and stabilizes reaction intermediates which perchance proceed to form reaction products (JOHNSTON, 2002). That said, the analysis of the conformations of these transition metals clusters becomes paramount for the development of new catalysts. The research of core-shell arrangement of nanomaterials, for example, have large relevance because its physico-chemical properties can be altered by change in size, composition and structure (RANJAN; CHAKRABORTY, 2021).

2.2 Electroreduction CO₂

Adsorption is when a molecule in the gas phase or in solution binds to atoms on the surface. The molecule that binds is called adsorbate, and the surface to which it binds is the adsorbent and the adsorption is commonly a main first step in heterogeneous catalysis. Then, understanding the adsorption process becomes important, because it helps to control the catalysis of a chemical reaction.

In the catalysis process, the properties of metals can be modified and refined through alloying, i.e., forming bimetallic solids. The same goes for nanoparticles and clusters. We know that in chemical processes, yields of one hundred percent are difficult, since losses occur during the process, and in catalysis it is not different, so its relevant synthesizing $A_{core}B_{shell}$ nanocatalysts, where A is a relatively inexpensive metal, which is (generally) less catalytically active, and B is more expensive, in order to decrease the process costs

(FERRANDO; JELLINEK; JOHNSTON, 2008).

The most commonly explored electrocatalysts for CO₂ electroreduction are transition metals, this is because these metals have vacant orbitals and active *d* electrons (QIAO et al., 2014). Among these transition metals, one of the most used metals in CO₂RR is copper, as it is capable of converting CO₂ into more than thirty different hydrocarbons and alcohols (NABI et al., 2022).

According to Woldu et al. (2022) the reduction process is guided by a multi-step-based coordination chemistry for the formation the following products CO, CH₃OH, CH₄, C₂H₄ and C₂H₅OH respectively. And the reaction can be understood involving four important steps, which are: CO₂ chemisorption on the electrocatalytic surface, ii) cleavage of C-O bond or formation of C-H bonds through electron transfer and/or proton coupling and other further reduced species, iii) C-C bond generation, the most challenging step, to form different hydrocarbons and oxygenates, and iv) rearrangement of product configuration to desorb from the electrocatalyst surface and diffuse into the electrolytic solution.

The mechanism propose for the reduction of CO₂ and the the interactions with the reaction intermediates are shown in Figure 3.

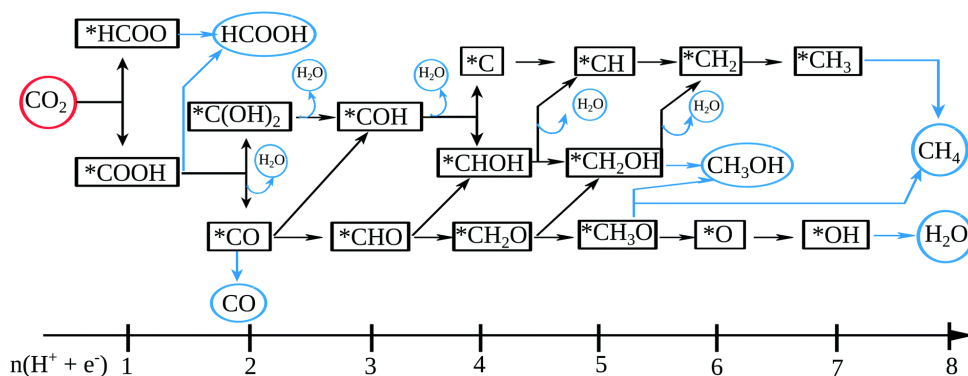


Figure 3 – Possible reaction pathways for CO₂ reduction through a sequence of proton-coupled electron transfer (PCET). The reactant, CO₂, is highlighted in red, adsorbed species in black, and other molecules involved in the reactions in blue. The * in the molecules means the adsorbed species.

Source: (VERGA et al., 2022)

2.3 Quantum Chemistry

Quantum mechanics is the extension of classical ideas into the behavior of subatomic, atomic, and molecular species. Nowadays, quantum mechanics forms the base about which all chemistry is built, being used to explain atomic structure and molecular bonding. According to this theory, particles are not localized at specific points in space, and may present both

wave and particle behavior. Thus, systems of particles can be completely portrayed as wave functions that characterize all their properties. Such wave functions are mathematical representations of the quantum states of a particle set, the properties of which correspond to quantum mechanical operators (MCQUARRIE, 2008).

2.3.1 Born-Oppenheimer Approximation

The Hamiltonian operator for a molecule or cluster may be described as:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon r_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_j \sum_{i > j} \frac{e^2}{4\pi r_{ij}} \quad (1)$$

We are going to consider a molecular system and assume the nuclei and electrons to be point masses, neglecting spin-orbit and other relativistic interactions. m_{α} and m_e represent the mass of the nucleus and the mass of the electron, respectively. $\hbar$ is the reduced Planck constant. The symbols α e β describe to the nuclei and the subscripted i e j denote the electrons. The first term in eq. 1 is the operator for the kinetic energy of the nuclei, with atomic numbers Z_{α} and Z_{β} . The second term indicates the operator for the kinetic energy of the electrons. The third term shows the potential energy of the repulsions between the nuclei, being $r_{\alpha\beta}$ the distance between nuclei α and β . The fourth term is the potential energy of attractions between the electrons and the nuclei, $r_{i\alpha}$ represent the distance between electron i and nucleus α . The last term is the potential energy of the repulsions between the electrons, r_{ij} being the distance between electrons i and j . The zero level of potential energy for eq. 1 corresponds to having all the charges, of electrons and nuclei, infinitely distant one of the far from one another (LEVINE, 2013).

The wave functions and energies of a molecule can be found from the time-independent Schrödinger equation:

$$\hat{H}\psi(q_i, q_{\alpha}) = E\psi(q_i, q_{\alpha}) \quad (2)$$

where (q_i and q_{α}) symbolize the electronic and nuclear coordinates, respectively.

Considering that the mass of the nuclei is greater than the mass of electrons ($m_{\alpha} \gg m_e$), we can assume that electrons will move much faster than nuclei. Therefore, a good approximation to electrons would assume that nuclei could be considered fixed while electrons would perform their motions. Taking into account the classical analogy, the time of one cycle of electronic motion, the change in nuclear configuration is negligible. Thus, considering the nuclei as fixed, we can hide the nuclear kinetic energy terms from eq. 1 to obtain the Schrödinger equation for electronic motion (LEVINE, 2013):

$$(\hat{H}_{el} + V_{NN})\psi_{el} = U\psi_{el} \quad (3)$$

The energy U is the electronic energy including internuclear repulsion. The internuclear distances $r_{\alpha\beta}$ is fixed. The purely electronic Hamiltonian $\hat{H}_{el}$ may definite as:

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_j \sum_{i>j} \frac{e^2}{4\pi r_{ij}} \quad (4)$$

The electronic Hamiltonian including nuclear repulsion is $\hat{H}_{el} + V_{NN}$. The nuclear-repulsion term V_{NN} is:

$$V_{NN} = \sum_{\alpha} \sum_{\beta>\alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon r_{\alpha\beta}} \quad (5)$$

The Schrödinger eq. (1) provides a set of electronic wave functions and electronic energies. For each nuclear configuration (obtained by changing the nuclear coordinates) this equation, can be solver. Each member of the set corresponds to a different molecular electronic state. The quantity V_{NN} is independent of these coordinates and is a constant for a given nuclear configuration, so we can hide this term from the equation 3 and consider only purely electronic energy (LEVINE, 2013)

$$\hat{H}_{el}\psi_{el} = E_{el}\psi_{el} \quad (6)$$

U and E_{el} are related by:

$$U = E_{el} + V_{NN} \quad (7)$$

As the energy (E) does not depend on any coordinates, the expressions for the nuclear motion and its Hamiltonian respectively are (LEVINE, 2013):

$$\hat{H}_N\psi_N = E_N\psi_N \quad (8)$$

$$\hat{H}_N = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 + U(q_{\alpha}) \quad (9)$$

This equation describes the dynamics of the nuclei by means of eigenvectors (nuclear wave function).

The approximation of separating electronic and nuclear motions is called the Born-Oppenheimer approach. The mathematical treatment of Born and Oppenheimer showed that the molecular wave function is satisfactorily approximated as (LEVINE, 2013):

$$\psi(q_i; q_\alpha) = \psi_{el}(q_i; q_\alpha) \psi(q_\alpha) \quad (10)$$

if $(\frac{m_e}{m_\alpha})^{\frac{1}{4}} \ll 1$. The Born-Oppenheimer approximation inserts few errors into the ground electronic states of molecules. The corrections for excited electronic states are higher than for the ground state, but they are still small compared to the errors introduced by the approximations used to numerically resolve the Schrödinger electronic equation of a molecule of many electrons (LEVINE, 2013).

2.3.2 Density Functional Theory

Many-body problems are defined as the difficulty of finding an exact solution to the Schrödinger equation, this due to the Coulomb pair interactions. A very effective method to reduce the many-body problem to a self consistent single-particle model is provided by density functional theory (DFT) (MARTIN, 2011).

2.3.2.1 The Hohenberg-Kohn Theorem

The hamiltonian of a molecular system, with M nucleus and N electrons, using the Born-Oppenheimer approximation and disregarding the relativistic effects is given by:

$$\hat{H} = - \sum_i^N \frac{1}{2} \nabla_i^2 - \sum_A^M \sum_i^N \frac{Z_A}{|R_A - r_i|} + \sum_{i < j}^N \sum_j^N \frac{1}{|r_i - r_j|} + \sum_{B < A}^N \sum_A^M \frac{Z_A Z_B}{|R_A - R_B|} \quad (11)$$

in which i and j represent electrons; A and B, represent the atomic nucleus; r_i and R_A , the coordinates of electron i and nucleus A respectively; Z_A the atomic number of A atom. The first term of this equation represents the kinetic energy operator, the third and fourth terms represent the electron-electron repulsion operator and nuclei-nuclei respectively, including the coulombic repulsion and all non-classical terms (exchange and correlation); the second term $\hat{U}$ represents the external potential related to electrons, which can be described by:

$$\hat{U} = \sum_i^N \sum_A^M - \frac{Z_A}{|R_A - r_i|} = \sum_i^N v(r_i) \quad (12)$$

The external potential $v(r_i)$ and the number of electrons N are specified, both define the quantum problem, that is, the electronic ground-state wave functions, allowed energies of

the molecule and properties of system are determined as the solutions of the electronic Schrödinger equation. The ground-state density can be deduced by solving the Schrodinger equation through ground-state wave function.

The electronic density is defined as:

$$\rho(r) = \int \dots \int \Psi(r_1, r_2, \dots, r_N)^* \hat{H} \Psi(r_1, r_2, \dots, r_N) dr_1 dr_2 \dots dr_N \quad (13)$$

in which $\Psi(r_1, r_2, \dots, r_N)$ is the fundamental state solution of the Hamiltonian. The total energy of the system, can be expressed as:

$$E_0 = \int \Psi(r_1, r_2, \dots, r_N)^* \hat{H} \Psi(r_1, r_2, \dots, r_N) dr_1 dr_2 \dots dr_N = \langle \Psi | \hat{H} | \Psi \rangle \quad (14)$$

The external potential can be separated in a functional of electronic density, then the total energy will be:

$$E_0 = \langle \Psi | \hat{T} + \hat{V}_e | \Psi \rangle + \int \rho(r) v(r) dr \quad (15)$$

The first theorem of Hohenberg-Kohn (HK) shows that for systems with a nondegenerate ground state, the ground-state electron probability density determines the external potential, that is, the external potential is a unique functional of electronic density in the ground state, as such the electronic density of a system determine the external potential and the number of electrons, and therefore the hamiltonian of the system (MORGON; COUTINHO, 2007).

The energy of the system is calculated through the Schrödinger equation, and the energy of an electronic system is determined by the electron density:

$$E = E_v[\rho] \quad (16)$$

The subscript v indicates the dependence on the external potential.

The second theorem establishes that the ground-state electron density minimizes the energy functional. Hohenberg-Kohn proved that for either electronic density (ρ_{tr}) approximation that satisfies $\int \rho_{tr}(r) dr = N$ and $\rho_{tr} \geq 0$ for all r , the following inequality holds: $E_0 \leq E_v[\rho_{tr}]$. E_v is the energy functional.

$$F[\rho] = \langle \Psi_{tr} | \hat{H} | \Psi_{tr} \rangle = \left\langle \Psi_{tr} \left| \hat{T} + \hat{V}_e + \sum_{i=1}^N v(r_i) \right| \Psi_{tr} \right\rangle \geq E_0 = E_v[\rho_0] \quad (17)$$

The ground-state energy is a density functional and will be minimal in the ground state when we find a ground state density, so the total energy will always be greater than or equal to the exact energy of the system.

These two Hohenberg- Kohn theorems show that ρ_{tr} defines its own $v_{tr}(r)$ and the hamiltonian $\hat{H}_{tr}$ and $\Psi_{tr}(r_1, r_2, \dots, r_N)$. The function $\Psi_{tr}(r_1, r_2, \dots, r_N)$, can be used as a trial function to the system with external potential. According to the variational principle:

$$E_0 = E_v[\rho] = F[\rho] + \int \rho(r)v(r)dr \leq E_v[\rho_{tr}] = F[\rho_{tr}] + \int \rho_{tr}(r)v(r)dr \quad (18)$$

With these theorems, we can conclude that all properties of a system with many bodies are determined by density of the ground-state and each property is functional of density of the ground-state and a functional maps a function to a result (MORGON; COUTINHO, 2007).

2.3.2.2 Kohn-Sham Equations

Kohn-Sham equations can be explained as being a Schrödinger equation for a fictitious system composed of non-interacting particles, this makes the original problem of many bodies be replaced by an electronic problem of independent electrons. The electron density must be the same as the original real system composed of real interacting particles.

The total energy can be expressed as a functional of the local electron density $\rho(r)$, as show in the eq. 19:

$$E[\rho] = T_s[\rho] + E_{xc}[\rho] + \int \left\{ V_1(r)\rho(r) + \frac{1}{2}\rho(r)V_H(r) \right\} d^3r + E_I \quad (19)$$

where $T_s[\rho]$ is the kinetic energy of non-interacting fermions, $E_{xc}[\rho]$ is the exchange-correlation energy (including a kinetic part) which is normally assessed within the local density approximation (LDA), and $V_H(r)$ is the direct (Hartree) Coulomb energy of the electrons given by (MARTIN, 2011):

$$V_H(r) = e^2 \int \frac{\rho(r')}{|r - r'|} d^3r' \quad (20)$$

In order to ease the problem of a system with many electrons, we will consider only the valence electrons for solving the equations. The core electrons are accounted for with pseudopotentials, and the nucleus and core electrons together are hereafter named as ions. We can do this, because the core electrons are those that are strongly bound to the nucleus, whereas the valence electrons make chemical bonds possible.

In eq. 19, E_I means the electrostatic energy of the ions; even if it does not depend on electronic density, it is incorporated in such a way that $E[\rho]$ in eq. 19 represents the total binding energy. The density $\rho(r)$ must be normalized to the total number Z of valence electrons (MARTIN, 2011):

$$\int \rho(r) d^3r = Z \quad (21)$$

Writing the electron density in terms of single-particle wavefunctions $\varphi(r)$ as:

$$\rho(r) = \sum_{i=1}^Z |\varphi(r)|^2 \quad (22)$$

the (non-interacting) kinetic energy functional $T_s[\rho]$ is explicitly known:

$$T_s[\rho] = \int \tau(r) d^3r = \int \frac{\hbar}{2m} \left\{ \sum_{i=1}^Z |\nabla \varphi_i(r)|^2 \right\} d^3r \quad (23)$$

The variation of the energy $E[\rho]$ with respect to the single-particle wavefunctions $\varphi_i^*(r)$

$$\frac{\delta}{\delta \varphi_i^*(r)} E[\rho(r)] = 0 \quad (24)$$

with the subsidiary condition that the $\varphi(r)$ be normalized, leads to the called Kohn-Sham (KS) equations:

$$\left\{ \hat{T} + V_{KS}(r) \right\} \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad (25)$$

$\hat{T}$ is the kinetic energy operator; the local potential $V_{KS}(r)$ is a sum of three terms:

$$V_{KS}(r) = V_{KS}[\rho(r)] = V_{xc}[\rho(r)] + V_H[\rho(r)] + V_I(r) \quad (26)$$

The first term is due to the exchange and correlation contributions:

$$V_{xc}[\rho(r)] = \frac{\delta}{\delta \rho(r)} E_{xc}[\rho] \quad (27)$$

$V_H(\rho)$ is the Hartree potential (20), and V_I is the ionic potential. The constants ε_i in (25) are the Lagrange multipliers employed to fix the norm of the i -th state (MARTIN, 2011).

The KS equations (25) evidence a self consistency problem, since the potential V_{KS} (26) depends on the density ρ and thus on the wavefunctions $\varphi_i(r)$ themselves; consequently they must be solved iteratively. With this simplification, it is clear the possibility to simultaneously treat the classical ionic motion with the quantum-mechanical motion of the electrons (MARTIN, 2011).

Chapter 3

Methodology

3.1 Theoretical Approach

The Vienna *ab initio* simulation package (VASP) (KRESSE; FURTHMÜLLER, 1996) is a computer program used for atomic scale materials modeling, e.g., electronic-structure calculations and quantum-mechanical molecular dynamics, on the basis of the first principles. VASP computes an approximate solution to the many-body Schrödinger equation, using density-functional theory (DFT), solving the Kohn-Sham (KS) equations, or within the Hartree-Fock (HF) approximation, solving the Roothaan equations.

Density functional theory (DFT) calculations were carried out with the Vienna *ab initio* simulation package (VASP) (KRESSE; FURTHMÜLLER, 1996). The generalized gradient approximation (GGA) functional in the Perdew-Burke-Ernzerhof (PBE) form was applied to consider exchange-correlation energies (PERDEW; BURKE; ERNZERHOF, 1996). The DFT-D3 method proposed by Grimme was used to include the dispersion interaction (GRIMME et al., 2010). The ion-electron interactions were described by the projected augmented wave (PAW) method (BLÖCHL, 1994). Table 1 shows the details of the Projector Augmented Wave (PAW) projectors. ENMAX specifies the recommended plane-wave cutoff energy in eV and Z_{val} provides the number of valence electrons on each element. The PBE exchange-correlation functional (PERDEW; BURKE; ERNZERHOF, 1996) was employed.

Table 1 – Technical details of the PAW-PBE projectors selected for this study. Recommended cutoff energy for the plane-wave basis set (ENMAX), number of valence electrons, (Z_{val}), and valence electronic configuration.

Element	PAW projector	ENMAX(eV)	Z_{val}	Valence
O	O_GW 19Mar2012	434.431	6	$2s^2 2p^4$
Cu	Cu_GW_new 19Mar2012	417.039	11	$3d^{10} 4s^1$
C	C_GW_new 19Mar2012	413.992	4	$2s^2 2p^2$
Co	Co_GW 31Mar2010	323.400	9	$3d^7 4s^2$
H	H_GW 21Apr2008	300.000	1	$1s^1$

3.1.1 Computational Parameters

For all calculations, the unit cell size was chosen such as to ensure a vacuum thickness of at least 15 Å in all directions to ensure negligible interaction among periodic images. A single **k**-point (the Γ point) was used for the Brillouin zone integration.

As we explored a large number of possible adsorption sites, preliminary cost-effective calculations were first performed for a initial exploration of the possible configuration (screening part). However, the final results reported in this work employed more rigorous convergence criteria and cutoff energies. Hereafter, we will refer to two types of calculations (screening and final), which employed different parameters, and are detailed below.

3.1.2 Screening Calculations

Screening calculations were performed such as to explore a larger number of adsorption configurations with lower computational cost. These calculations were carried out with a reduced cutoff energy of 380.127 eV, which is 12.25 % lower than the recommended value (ENMAX) for oxygen. For all calculations in this step, a convergence criterion of 1.0×10^{-4} eV was used for the total electronic energy and $0.10 \text{ eV}\text{\AA}^{-1}$ for the atomic forces on all atoms. The atomic positions of the cluster have been fixed, and only the coordinates of the molecule were optimized.

3.1.3 Final Calculations

The final calculations were performed with a cutoff energy of 488.735 eV, which is 12.25 % higher than the recommended value (ENMAX) for oxygen. For all calculations in this step, a convergence criterion of 1.0×10^{-5} eV was used for the total electronic energy and $0.025 \text{ eV}\text{\AA}^{-1}$ for the atomic forces on all atoms. All atoms in the unit cell were fully relaxed.

3.2 Unary and Dopped Cu₅₅ Nanoclusters

3.2.1 Unary Structures

The first step of this work consisted in the determination of the lowest energy structure of the Cu₅₅ nanocluster without the adsorbed molecules. To do so, several geometries of 55-atom metal clusters (see reference [Piotrowski et al. \(2016\)](#)) were used as candidates for the calculations and optimized. For each geometry, calculations with and without employing van der Waals corrections were performed for the search of the most stable structure.

3.2.2 Doped Cluster

After choosing the Cu₅₅ structure with lowest energy, one copper atom is replaced by a cobalt atom. The choice of the replacement position took into account the different effective coordination number (*ECN*).

3.2.3 Effective Coordination Number (*ECN*)

ECN is an useful generalization of the classical definition of coordination number (number of nearest neighbors of an atom); it considers the length of the bonds ([HOPPE, 1979](#)). In the effective coordination concept, a different weight is calculated for each bond length d_{ij} by using a weight function, i.e., $w_{ij} \neq 1.0$ for all ij pairs. All w_{ij} are calculated with respect to the atom weighted bond length, d_{ij}^i , which must be calculated for each atom i ([DA SILVA, 2011](#)). This approach is based on the fact that a particular atom i binds stronger with the closer j atoms, and hence, small changes in the coordination environments can be taken into account ([DA SILVA et al., 2010](#)). The ECN_i is obtained by the following set of equations:

$$ECN_i = \sum_j \exp \left[1 - \left(\frac{d_{ij}}{d_{av}^i} \right)^6 \right] \quad (28)$$

where d_{ij} is the distance between atom i and j , while d_{av}^i is defined as:

$$d_{av}^i = \frac{\sum_j d_{ij} \exp \left[1 - \left(\frac{d_{ij}}{d_{av}^i} \right)^6 \right]}{\sum_j \exp \left[1 - \left(\frac{d_{ij}}{d_{av}^i} \right)^6 \right]} \quad (29)$$

The average *ECN* and d_{av} for a particular set of atoms can be obtained by

$$ECN = \frac{1}{N} \sum_{i=1}^N ECN_i \quad (30)$$

where N is the number of atoms.

As the *ECN* is obtained by the sum of all weights it is not necessarily an integer value. Thus, this concept can be applied for symmetric or distorted structures consistently.

3.3 Adsorption of CO₂ Reduction Intermediates

Starting with the optimized geometry of the cluster, the adsorbate molecules were positioned on the top, bridge and hollow sites (as shown in Figure 4) and considering different molecule orientations.

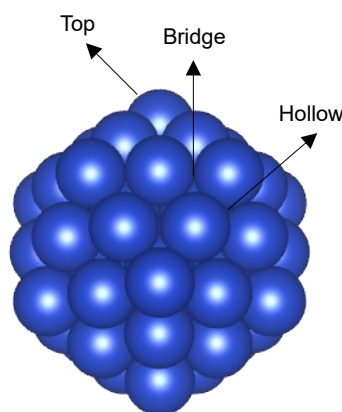


Figure 4 – Cu₅₅ nanocluster showing the top (above atom), bridge (above middle point of 2 atoms) and hollow (above middle point of 3 atoms) sites.

In order to understand the interaction between CO₂ reduction intermediates, the adsorption of H, OH, CO, COH and HCO will be analyzed in doped and non-doped nanoparticles.

3.3.1 H, OH and CO

For the H atom and the OH and CO molecules the adsorption sites were defined taking into consideration half of the cluster, given its symmetry. In all, 26 sites were proposed to start the calculations, being 6 in the top position, 10 in the bridge, and 10 in hollow.

3.3.2 COH and HCO

The adsorption of molecules such as COH and HCO on Cu₅₅ clusters can generate a large number of nonequivalent adsorption sites due to the possible orientations of the adsorbates, including monodentated and bidentated configurations. To sample the various possible adsorption configurations, we employed the strategy described by [Zibordi-Besse et al. \(2016\)](#). Briefly, it works as follows: (i) We first select the structure of the cluster (Cu₅₅) and that of the molecule (COH or HCO). (ii) 100 million random adsorbed configurations are generated for the selected molecule on the Cu₅₅ cluster. (iii) To reduce our structural

database, similar or redundant structures are removed (as they can lead to the same local minimum structure upon the geometric optimization). Through the Euclidean distances, which is the distance between two vectors normalized by the sum of the module of the two vectors, it is possible to remove the dependence on the particle size, leaving only 5000 structures, which represent different regions in the potential energy surface. Afterwards these 5000 structures were further reduced to 50 using the K-means algorithm, described by [Schrier \(2020\)](#).

3.3.3 Energetic Analyses

We use the computational hydrogen electrode model (*CHE*) ([NØRSKOV et al., 2004](#); [PETERSON et al., 2010](#)) to evaluate free energy changes for the electrochemical steps.

The computational hydrogen electrode (CHE) approach proposed by [NØRSKOV et al.](#) represents a way of modeling electrochemistry by quantitatively incorporating insights from first-principles calculations. The CHE method enables the evaluation of the relative free energies of intermediates along an electrochemical reaction applying an electrical potential (U), in this case zero ($U = 0$) based on the reversible hydrogen electrode (RHE), according to reaction:



Equation 31 is defined to be in equilibrium at zero voltage, at all values of pH, at all temperatures, and with H_2 at 30 296 Pa pressure. Then, using the CHE we can calculate the chemical potential of a proton-electron pair, $\mu(H^+) + \mu(e^-)$ through the chemical potential of gaseous hydrogen $\frac{1}{2}\mu(H_2)$ at a potential of 0 V. Therefore, the chemical potential of the proton-electron pair can be adjusted taking into account the changing the energy of a proton-electron pair and a $-eU$ correction.

The reaction Gibbs free energy at $T = 298.15$ K was calculated using the following equation:

$$G = E_{tot} + ZPE + \int C_p dT - TS + E_{sol} \quad (32)$$

where E_{tot} is the electronic total energy calculated from the *DFT* calculations, ZPE is the zero point energy, $\int C_p dT$ the enthalpic temperature, $-TS$ the entropy corrections, and E_{sol} the solvation energy correction.

All of these thermal corrections ($ZPE + \int C_p dT - TS$) were obtained from the vibrational analysis implemented in VASP by using the harmonic oscillator approximation and the

thermochemistry module from the atomic simulation environment package ([LARSEN et al., 2017](#)) and the following equations:

$$ZPE = \sum_i \frac{1}{2} \varepsilon_i, \quad (33)$$

$$\int C_p dT = \sum_i \frac{\varepsilon_i}{e^{k_B T} - 1}, \quad (34)$$

$$S = K_B \sum_i \frac{\varepsilon_i}{K_B T (e^{k_B T} - 1)} - \ln(1 - e^{-\varepsilon_i/K_B T}), \quad (35)$$

where ε_i are the energies associated with the vibrational frequencies, k_B the Boltzmann constant, and T the temperature.

Chapter 4

Analysis and Discussion of Results

4.1 Lowest Energy DFT-PBE configurations

Nanoalloys can be classified according to their mixing pattern (also named chemical ordering) and geometric structure. For nanoalloys several structural types are possible. Having said that, the possibility to control the reactivity of transition-metal (TM) nanoparticles by tuning their size, shape, and surface termination provide the possibility to design new catalysts devices for a wide range of technological applications (DA SILVA et al., 2010). Therefore, the first stage of this work aimed the optimizations of different geometries of Cu_{55} using common structures found in unary clusters of 55 atoms (PIOTROWSKI et al., 2016): icosahedral, LOW, LOW-Au, *hexagonal close-packed wheel-type* (WHE), disordered reduced-core (DRC1 e DRC2), cuboctahedron (CUB) and fragment face-centered cubic (FCCf), as seen in Figure 5.

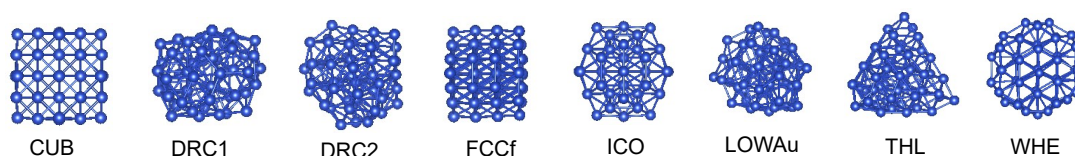


Figure 5 – Configurations obtained after optimization for Cu_{55} clusters . Lowest energies DFT-PBE configuration obtained for Cu_{55} .

The semi-local and hybrid functionals do not include the London dispersion forces, therefore they can not be applied reliably on systems where the London dispersion forces play an important role. To assess the impact of such forces, two calculations were performed to compare the energy values, one using the DFT-D3 correction method (GRIMME et al., 2010) and the other not. Figure 6 shows the results of the relative energies for the unary geometries of copper. For both results, the icosahedron (ICO) configuration presents the lowest energy, and therefore the most stable. This Figure also shows that the inclusion of

dispersion corrections increases the energy difference between any structure and the global minimum.

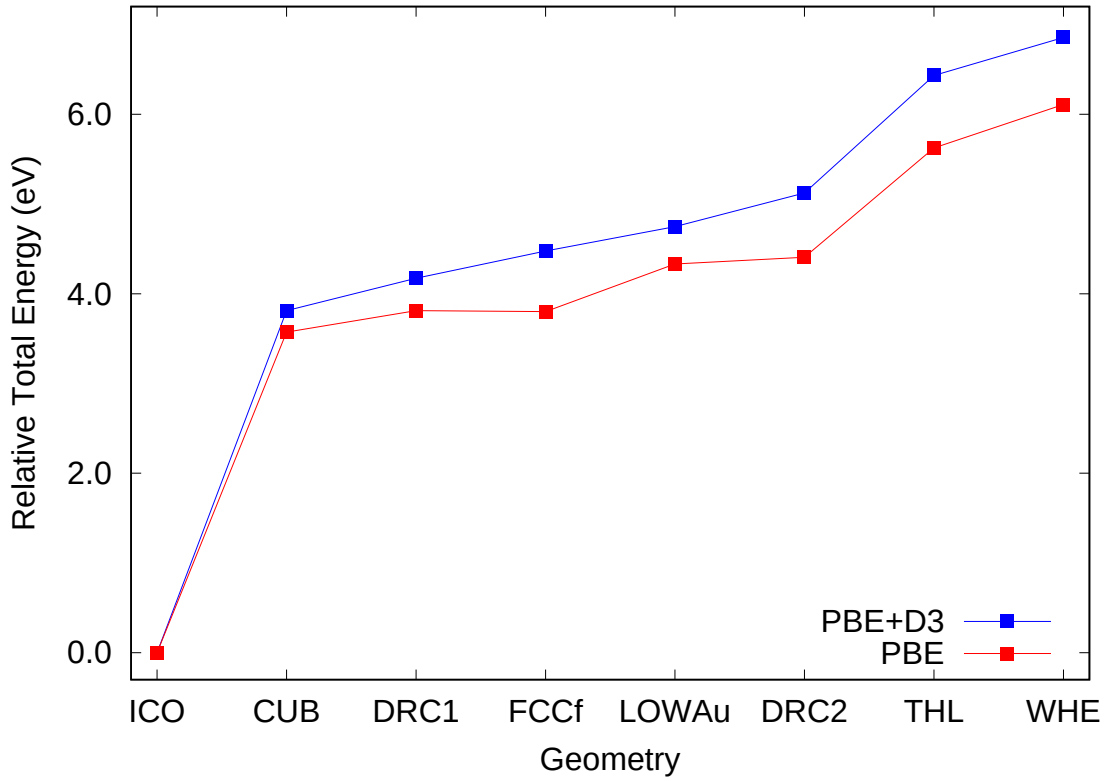


Figure 6 – Relative energies for different model structures including dispersion corrections (PBE+D3) and without its inclusion (PBE).

Figure 5 shows the configurations obtained after the optimization. The icosahedral structure, which is the most stable configuration has one atom in the geometric center and twelve encased in the core. The remaining forty-two atoms are located on the surface. Thus, the icosahedral geometry of unary copper was selected as the most stable structure and therefore used in the other calculations of this work. The dispersion corrections also will be taken into consideration.

4.1.1 Cobalt Doping Cu₅₅ Nanoclusters

The combination of two different elements in a cluster allows changing the total number of electrons independently of the total number of atoms. In this stage, one copper atom was replaced by one cobalt atom.

The icosahedron structure has five nonequivalent TM atoms as shown in Figure 7, in order to investigate the doping effect, the analysis of the ECN_i becomes important, since the cobalt atom will be replaced in one of the nonequivalent atoms. The ECN calculations show that there are 23 atoms in the M3 position with $ECN = 7.90$, this same ECN is also

observed for the 6 atoms in the M5 position, while for the M4 position there are 12 atoms with $ECN = 5.58$. For the atoms in the core, there are 12 atoms in the M2 position with $ECN = 12.21$ and one atom, in the core, with $ECN = 13.04$.

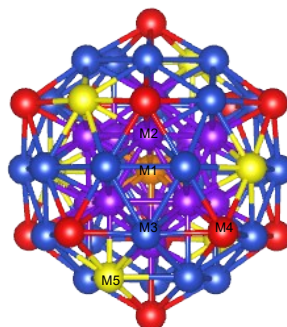


Figure 7 – Icosahedron structure with 55 atoms. The atoms are indicated with different colors to show the five nonequivalent atoms. 1 orange atom in the center (M1), 12 purples in the first shell (M2), blue (M3), red (M4), and yellow (M5) in the second shell composed of 42 atoms.

The energy of clusters is shown in Figure 8. The results show that the site with lowest energy is M2. For future calculations, the cobalt atoms in M2 and M4 positions were chosen. M2 position was chosen because it is in the core and has lower energy than M1 position, while the M4 position was chosen to represent the surface, and has lower energy than M3 and M5 positions.

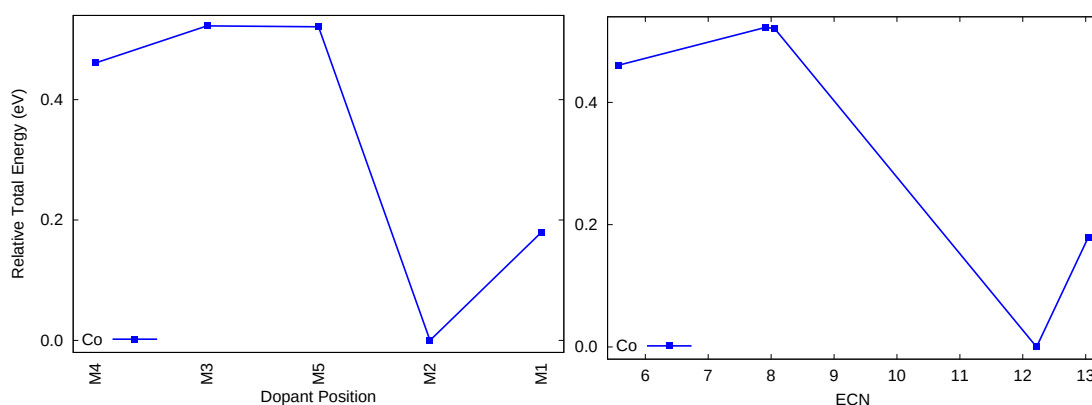


Figure 8 – Relative energies for different dopant positions and effective coordination number (ECN). (M1) and (M2) are located in the core, (M3), (M4) and (M5) are located in the third shell. The ECN in the positions M1, M2, M3, M4 and M5 are 13, 12.1, 7.9, 5.57, 8.05 respectively.

Figure 9 shows the configurations obtained after the optimization.

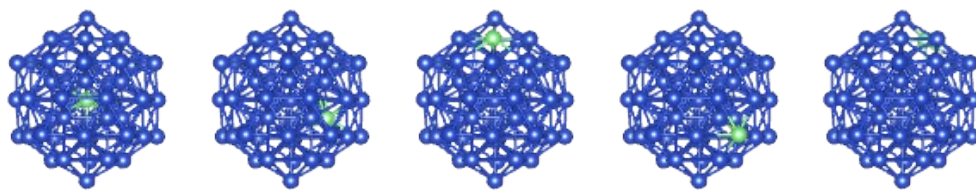


Figure 9 – Lowest energy DFT-PBE configurations obtained for Cu_{54}Co . The green atom represents the cobalt atom.

4.2 Adsorption Properties on Unary and Doped Cu_{55} Nano-clusters

4.2.1 Results of the Screening Calculations

As discussed in the methodology, in this work only the H, OH, CO, COH and HCO adsorbates will be considered. These adsorbates were chosen to describe the interactions of the molecular species involved in the reduction of CO_2 because they have a high energetic barrier according to the study of Verga et al. (2022). For each system, different orientations of adsorbates were tested. The results are presented below.

4.2.1.1 H Adsorption

For the H adsorption it is possible to observe a trend that after optimization the structure tends to be more stable in a hollow configurations, i.e, above the middle point of 3 atoms of copper. As can be seen in Figure 10 the hollow sites present the lowest energies, top the higher energies and bridge the intermediate. It can also be noted the presence of five energy plateaus, where the lowest energies are represented by the H8, B5, B2, T1 and T2 sites respectively. These structures are shown in Figure 11 and are selected for the final calculations, as discussed in the methodology section.

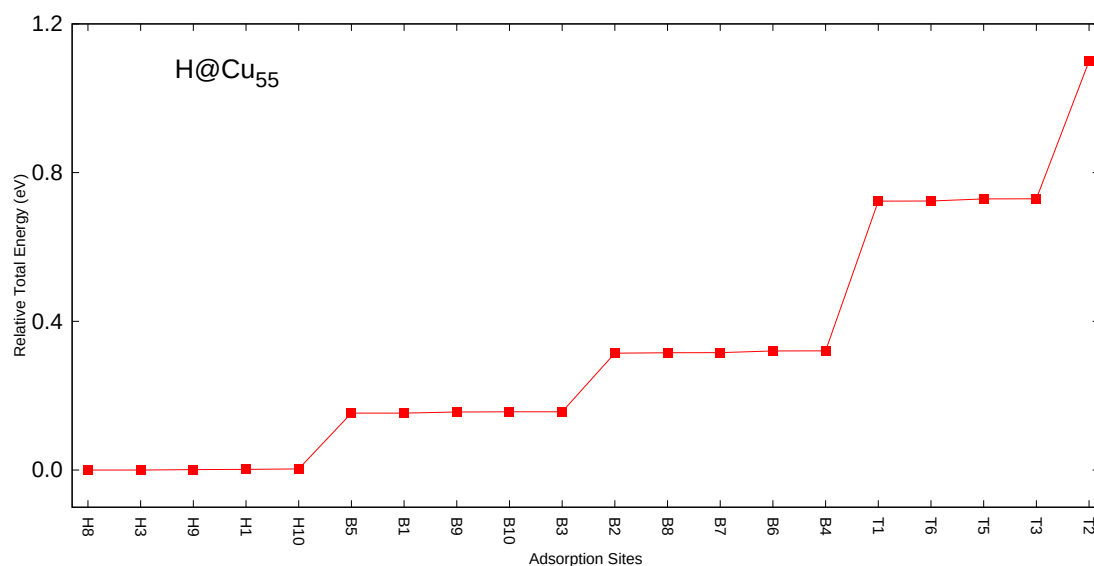


Figure 10 – Relative energies of the optimized H adsorption configurations on the Cu_{55} cluster. The most energetically stable configuration is used as reference.

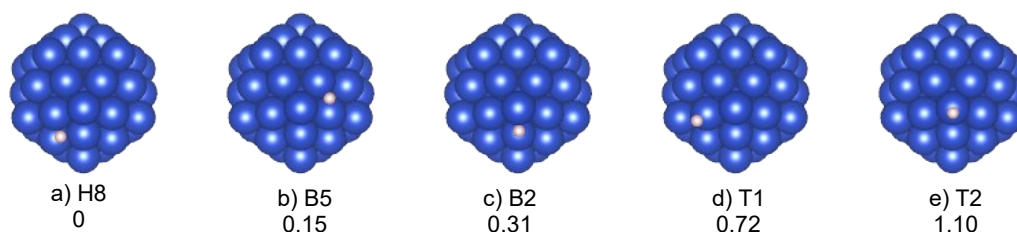


Figure 11 – Configurations obtained for H and Cu_{55} system and relative energies eV. The atoms in blue indicate Cu and the atom in white indicate H.

Figure 12 shows the shortest distance between the H atom and the Cu atom of the Cu_{55} cluster.

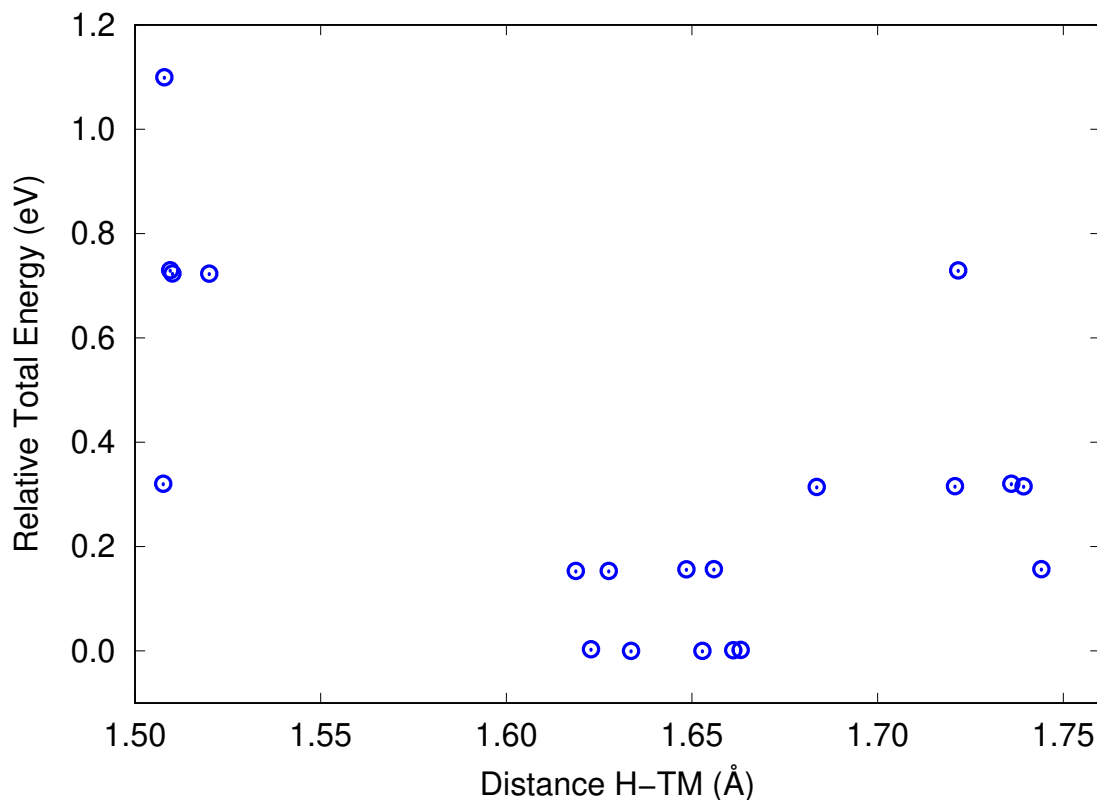


Figure 12 – Relative energies of the adsorbed configurations of an H molecule over the Cu₅₅ cluster as function of the shortest Cu–H distance.

4.2.1.2 OH Adsorption

For the OH adsorption, a clear preference for hollow or bridge sites cannot be observed, as their energies are quite similar. In Figure 13 all we can confirm is that the top sites show higher energies. It is noteworthy that in all systems the oxygen ends up bound to the cluster, even in cases where H atom begins closer to the cluster than the O at the beginning of the optimization.

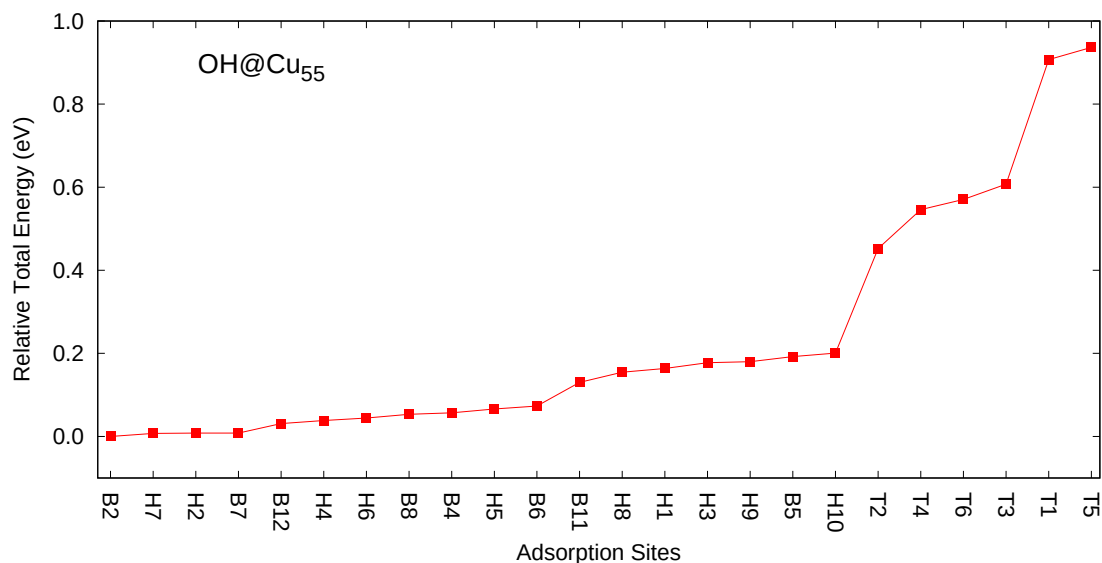


Figure 13 – Relative energies of the optimized OH adsorption configurations on the Cu_{55} cluster. The most energetically stable configuration is used as reference.

For OH adsorption, we can realize that there is no logical sequence as noted in the H adsorption. In that case, we chose the bridge and hollow sites of lower energies in each plateau, and two more top sites. Then, eight structures were chosen to perform the final optimization. These adsorption systems are shown in the Figure 14.

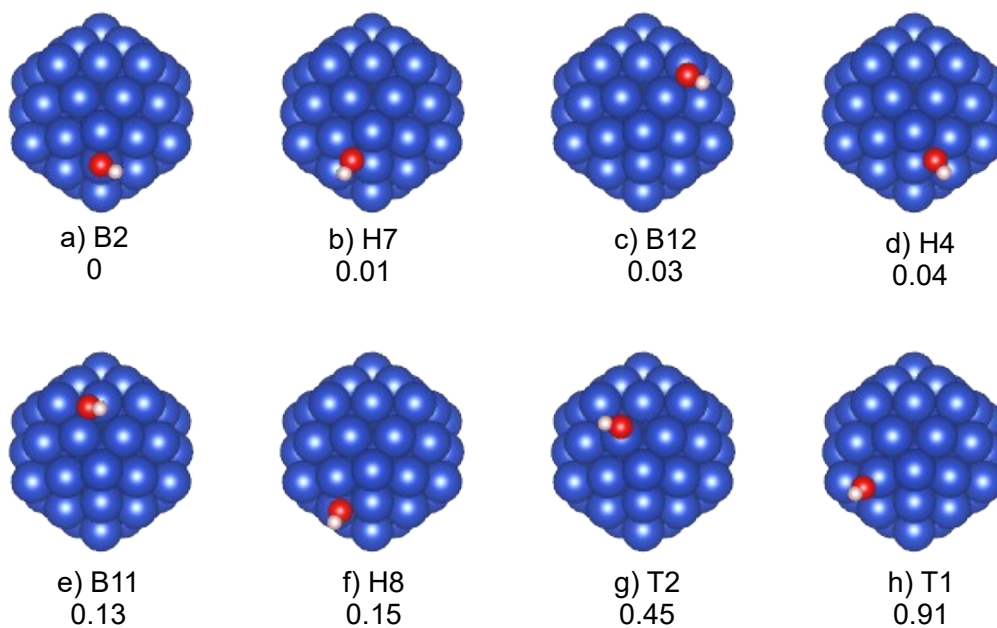


Figure 14 – Configurations obtained for OH and Cu_{55} system and relative energies eV. The atoms in blue indicate Cu and the atoms in red and white indicate O and H respectively.

Figure 15 shows the shortest distance between the O atom and the Cu atom of the Cu₅₅ cluster.

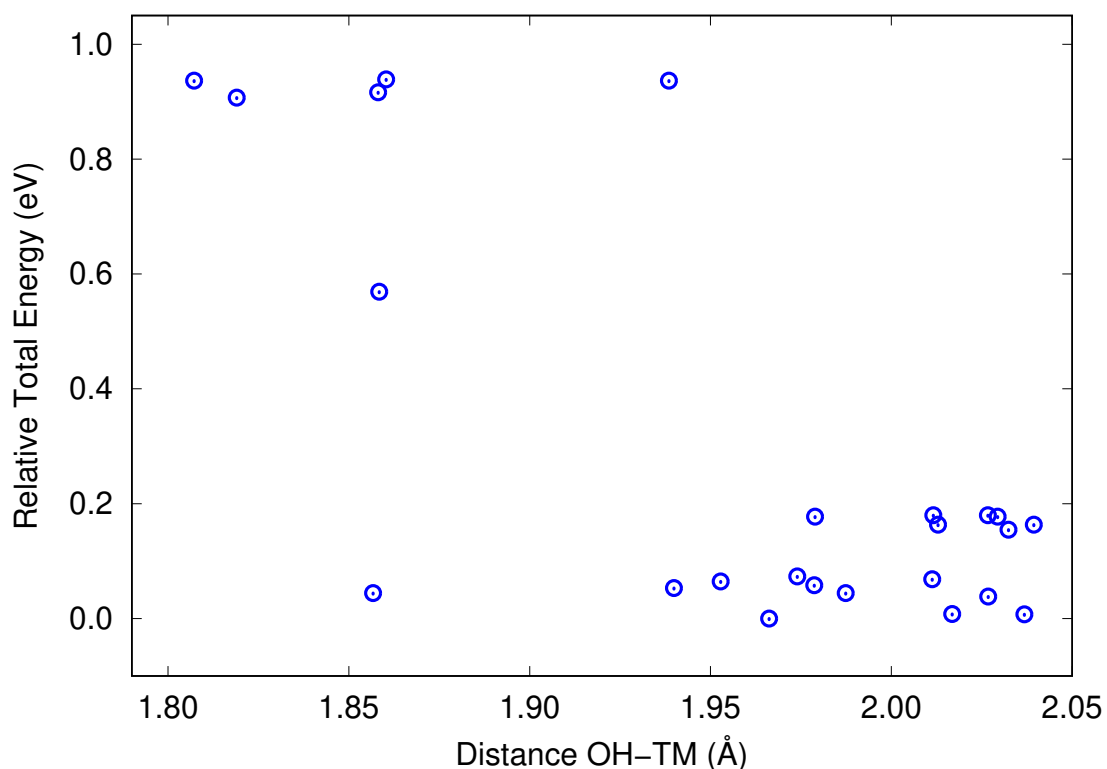


Figure 15 – Relative energies of the adsorbed configurations of an OH molecule over the Cu₅₅ cluster as function of the shortest Cu–O distance.

4.2.1.3 CO Adsorption

According to Figure 16, we can conclude that for CO adsorption the lowest energies are predominant in the hollow sites, followed by bridge and top sites. However, an exception is seen for the B6 site, which shows the highest energy. On all systems the C atom ends bound to the cluster.

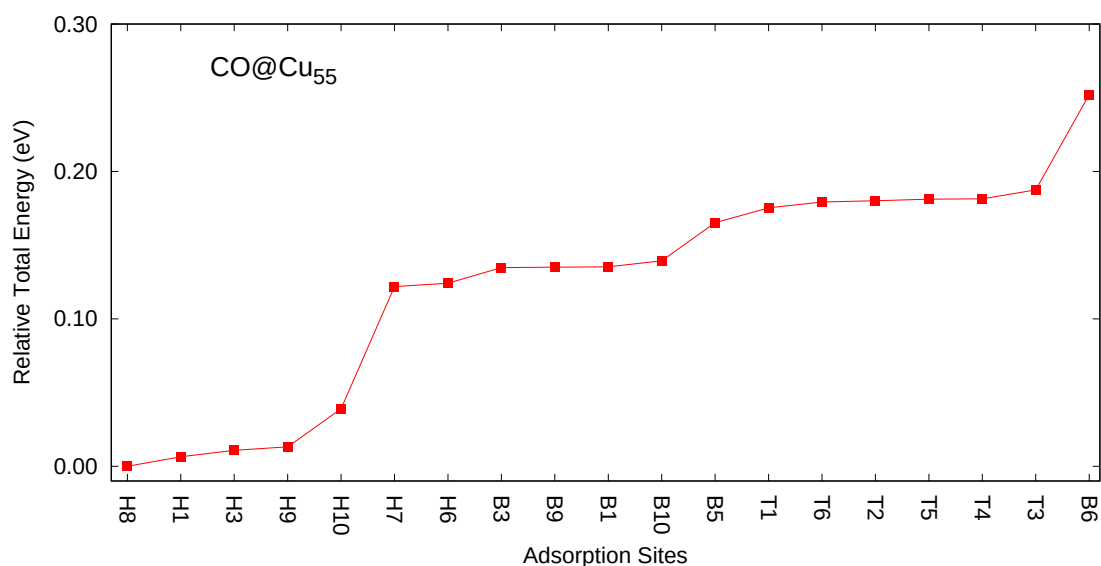


Figure 16 – Relative energies of the optimized CO adsorption configurations on the Cu_{55} cluster. The most energetically stable configuration is used as reference.

For the CO adsorption, eight structures were chosen to perform the final optimization following a criterion similar to that of OH adsorption. These adsorption systems are shown in Figure 17.

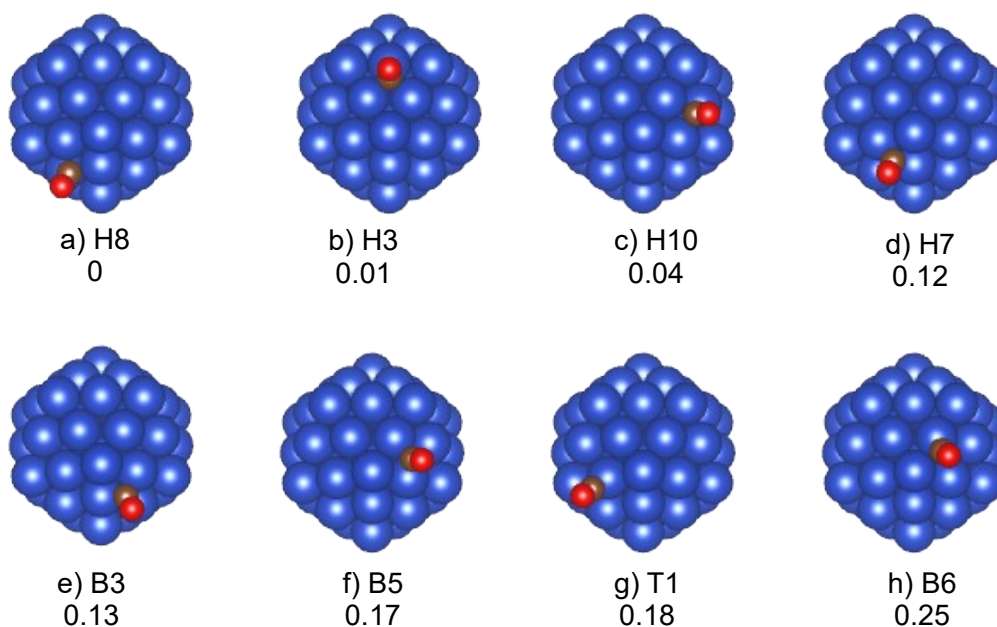


Figure 17 – Configurations obtained for CO and Cu_{55} system and relative energies eV. The atoms in blue indicate Cu and the atoms in brown and red indicate C and O respectively.

Figure 18 shows the shortest distance between the C atom and the Cu atom of the Cu_{55}

cluster.

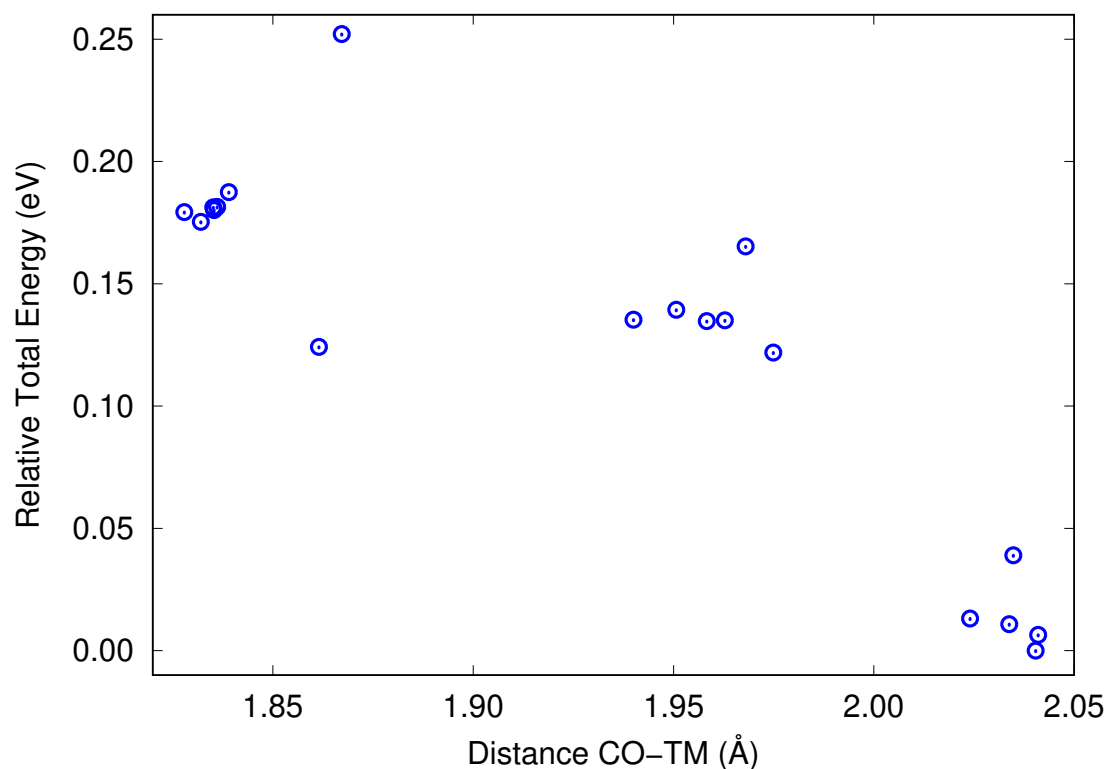


Figure 18 – Relative energies of the adsorbed configurations of an CO molecule over the Cu₅₅ cluster as function of the shortest Cu – C distance.

4.2.1.4 COH Adsorption

For the COH adsorption, according to Figure 19, it is possible to conclude that the lowest energies are predominant in the hollow sites, i.e, above the middle point of 3 atoms. The higher energies are in the top sites, indicating a preference of COH in the hollow sites. On all systems the carbon atom ends are bound to the cluster.

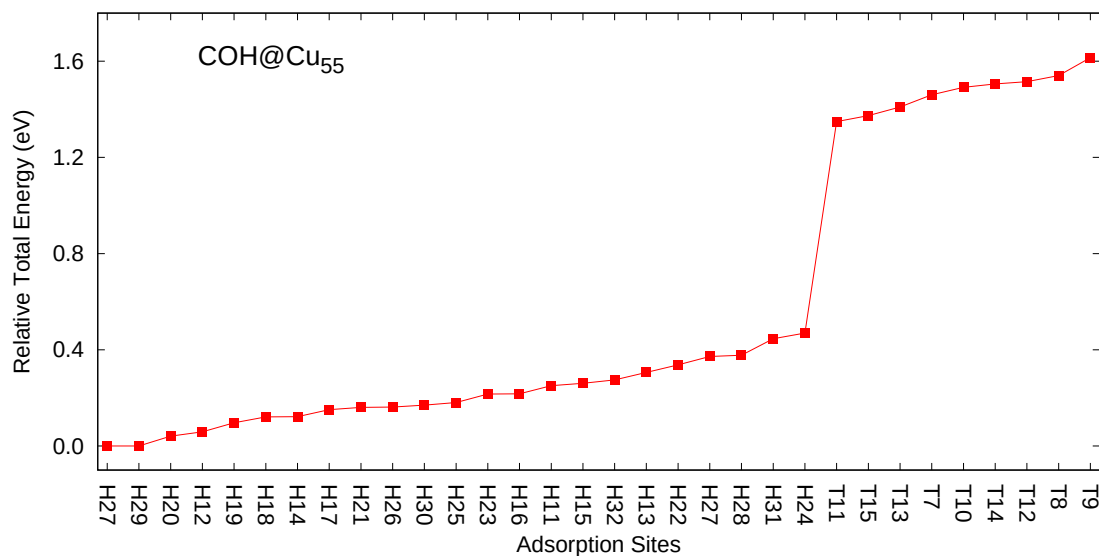


Figure 19 – Relative energies of the optimized COH adsorption configurations on the Cu_{55} cluster. The most energetically stable configuration is used as reference.

For the COH adsorption, ten systems were chosen to perform the final optimizations. In these adsorption systems, there are only hollow and top sites, with the highest number of hollow sites. The configurations selected for a subsequent final optimization are given in Figure 19. They were chosen such as to ensure diversity (by removing similar structures or energies) and provide low energy candidates.

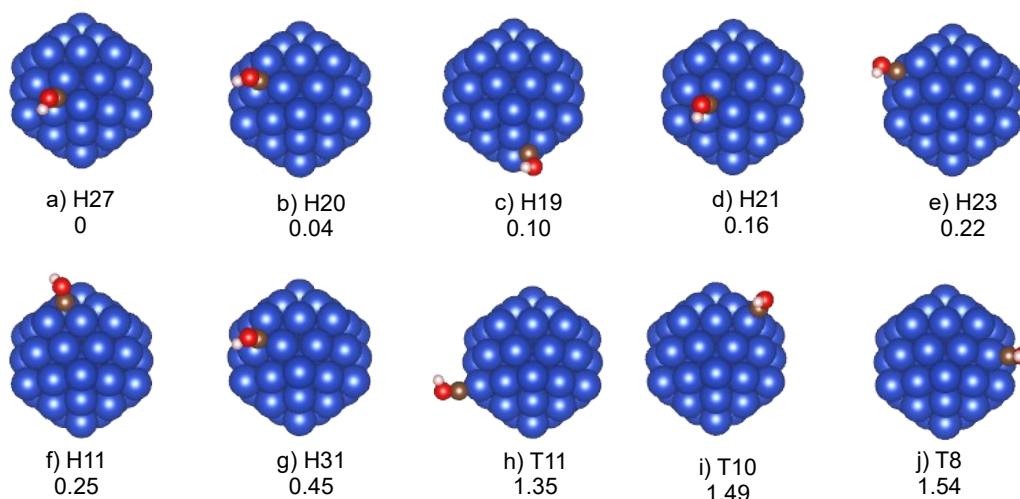


Figure 20 – Configurations obtained for COH and Cu_{55} system and relative energies eV. The atoms in blue indicate Cu and the atoms in brown, red and white indicate C, O and H respectively.

Figure 21 shows the shortest distance between the C atom and the Cu atom of the Cu_{55} cluster and the angle formed by C, O and H atoms after optimization.

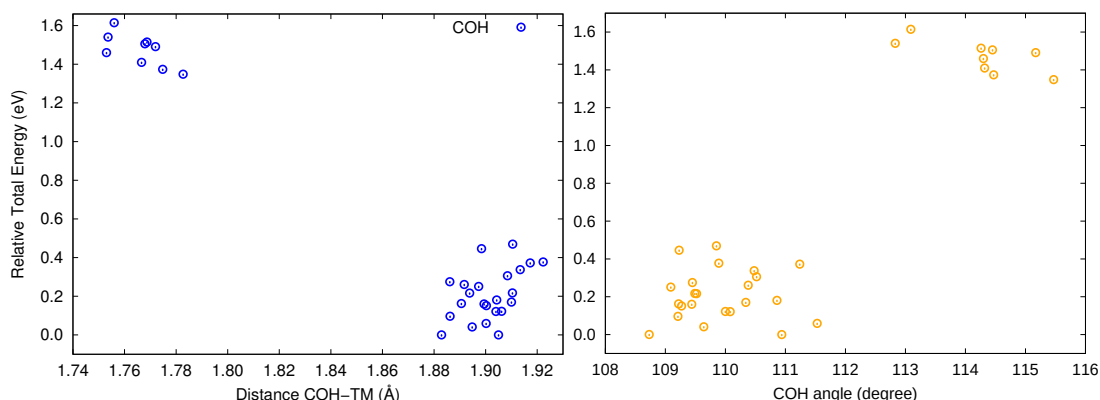


Figure 21 – Relative energies of COH adsorbed on the Cu_{55} cluster as function of the shortest Cu–C distance, and as a function of the angle formed by C, O and H atoms.

4.2.1.5 HCO Adsorption

The sites represented in Figure 22 with the symbols * and +, mean that after the optimization the structure ended with a bidentate geometry, in which the two atoms of the molecule are bound to the cluster. In the systems under study, the symbol * indicated in the sites, means that both the C atom and O atom after optimization, ended bound to the cluster while the symbol + indicates that both the C atom and H atom ended bound to the cluster. According to Figure 22, we can say that the B8* and B5* sites feature lowest energies and the top sites feature higher energies. In most cases, the C atom is bound to the cluster, except in T13 and T16, where the O ends are bound to the cluster.

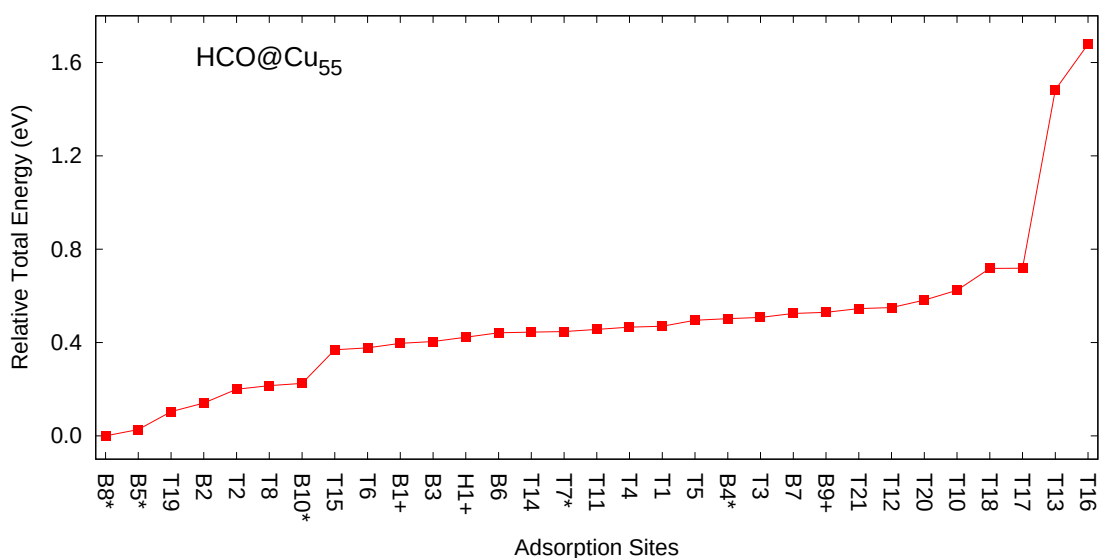


Figure 22 – Relative energies of the optimized HCO adsorption configurations on the Cu_{55} cluster. The most energetically stable configuration is used as reference.

For the HCO adsorption, ten structures were chosen to perform the final optimizations. In

these adsorption systems there are bridge and hollow sites with bidentate geometry. The choice of representative structures of this system took into account the different structural models after the optimization, trying to select the structures with lowest energies of the plateaus of the graph on Figure 22. The following systems were chosen B8*, B5*, B2, B10*, B1, H1+, T1, B7, T18 and T13. The adsorption systems chosen to perform the final optimization are shown in Figure 23.

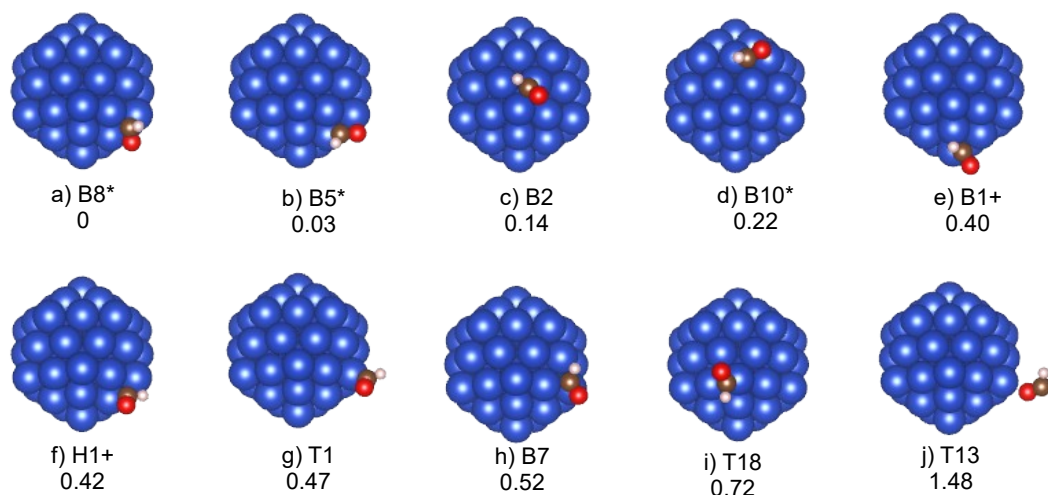


Figure 23 – Configurations obtained for HCO and Cu_{55} system and relative energies eV. The atoms in blue indicate Cu and the atoms in brown, red and white indicate C, O and H respectively.

Figure 24 shows the shortest distance between the C atom and the Cu atom of the Cu_{55} cluster and the angle formed by H, C and O atoms after optimization.

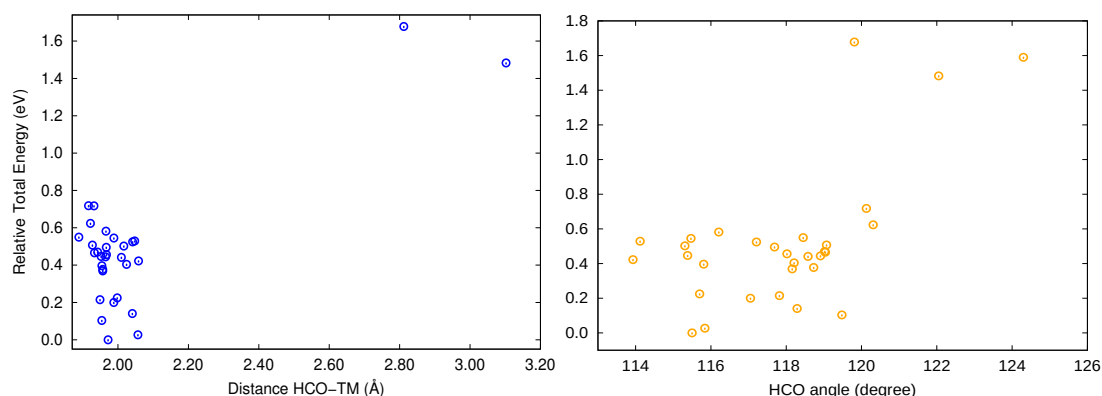


Figure 24 – Relative energies of HCO adsorbed on the Cu_{55} cluster as function of the shortest Cu–C distance, and as a function of the angle formed by H, C and O atoms.

4.2.2 Results of the Refined Calculations

The refined calculations on the structure in the previous section are now presented. It will be shown the results of the adsorption when the cluster is non-doped and cobalt-doped. For cobalt-doped clusters, two results will be discussed, the first when the cobalt atom is in the subsurface and the second when the cobalt atom is the surface to the cluster.

4.2.3 H Adsorption

For the H adsorption, according to Figure 25, we can see the most stable configurations are hollow, both for doped or non-doped cases.

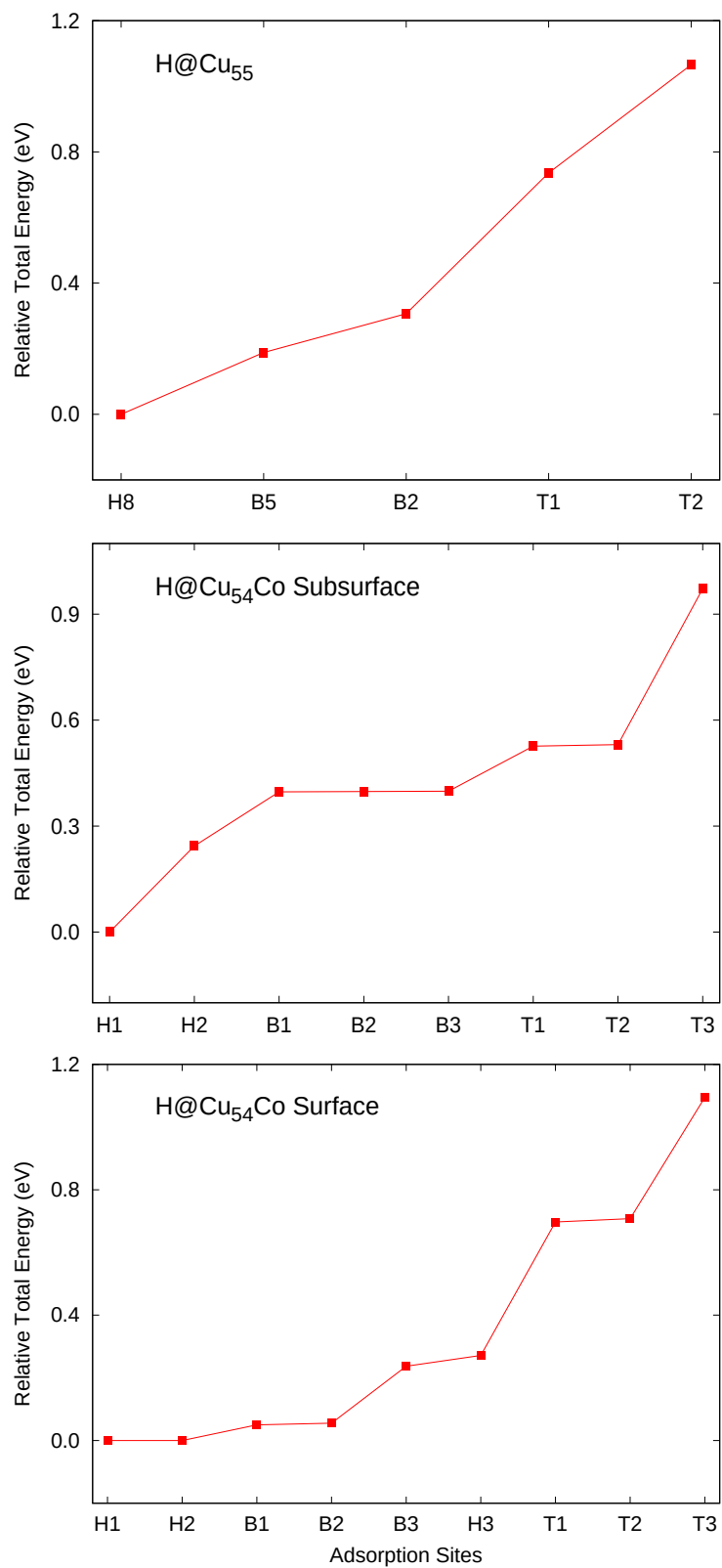


Figure 25 – Relative energies of the optimized H adsorption configurations on the Cu₅₅ and Cu₅₄Co clusters. The most energetically stable configuration is used as reference.

Figure 26 shows the adsorption sites, geometries and relative energy after optimization for

the adsorption of H on Cu₅₅ nanoclusters. The structures are in ascending order of energy.

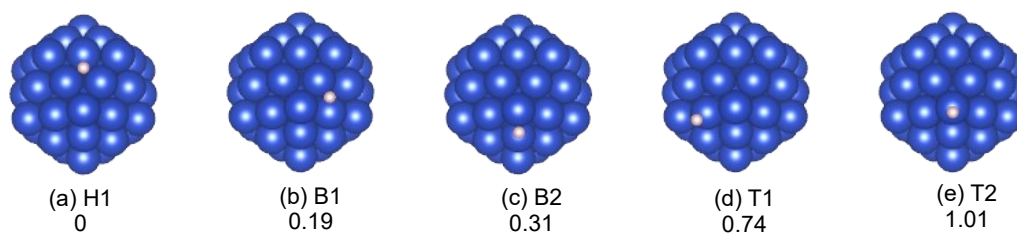


Figure 26 – Optimized configurations (H@Cu₅₅) after adsorption of H into Cu₅₅. Adsorption sites and relative energy eV.

Figures 27 and 28 show the adsorption sites, geometries and relative energy after optimization for the adsorption of H on Cu₅₄Co nanoclusters. The structures are in ascending order of energy.

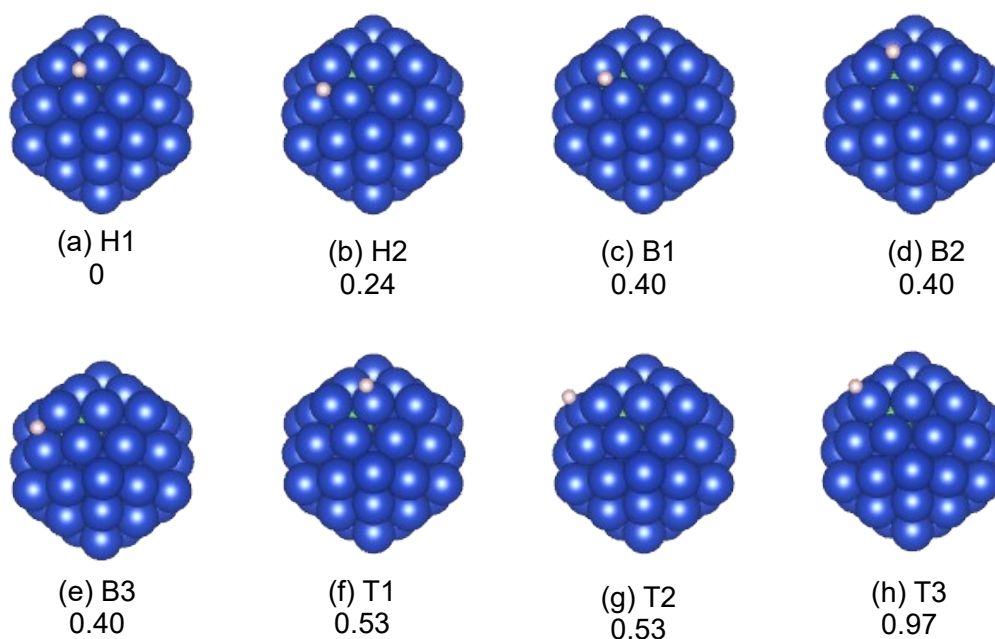


Figure 27 – Lowest energy structures (H@Cu₅₄Co) upon adsorption on the clusters in the subsurface position. Adsorption sites and relative energy eV.

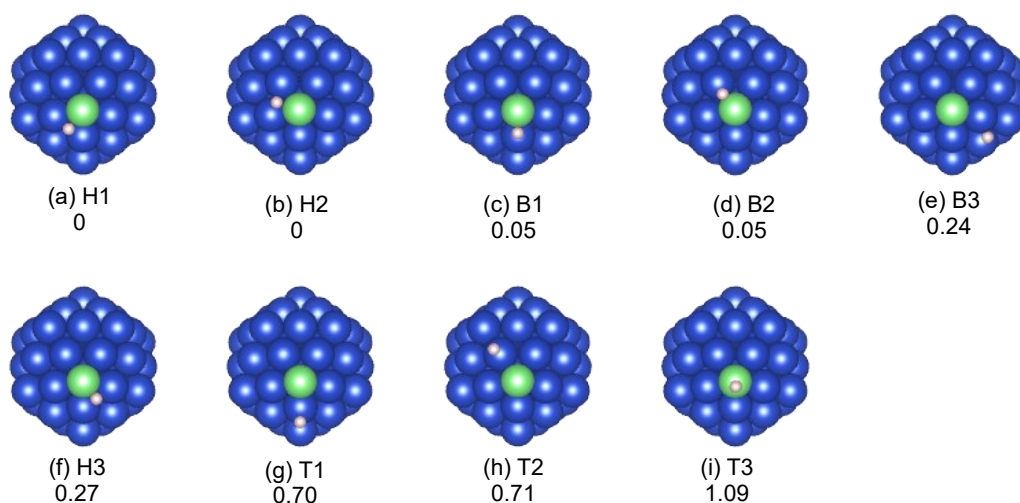


Figure 28 – Lowest energy structures ($\text{H@Cu}_{54}\text{Co}$) upon adsorption on the clusters in the surface position. Adsorption sites and relative energy eV.

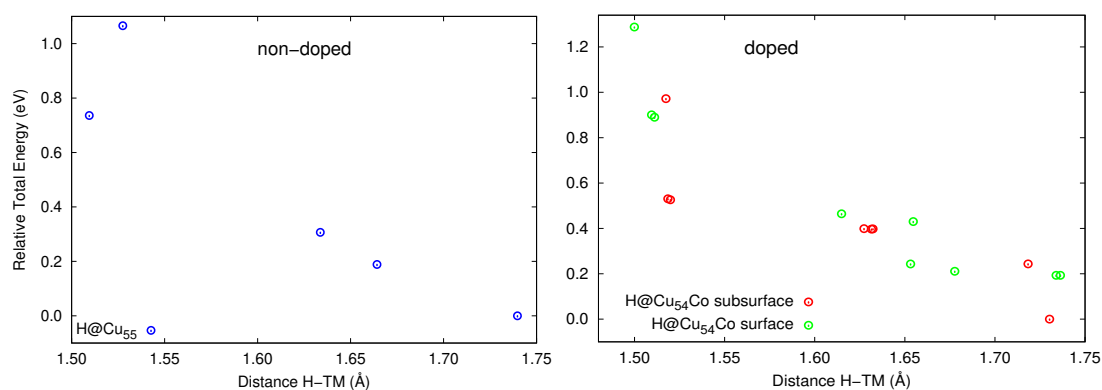


Figure 29 – Relative energies of the adsorbed configurations of an H molecule over the Cu_{55} cluster as function of the shortest Cu–H distance.

Figure 29 shows the shortest distance from the hydrogen atom to the cluster. The first in relation to the non-doped cluster and the second in relation to the doped cluster.

4.2.4 OH Adsorption

For the OH adsorption according to Figure 30, hollow configurations are the most stable when the cluster is not doped and when the dopant is in the surface. However, when the cobalt atom is in the subsurface, the bridge configuration is the most stable.

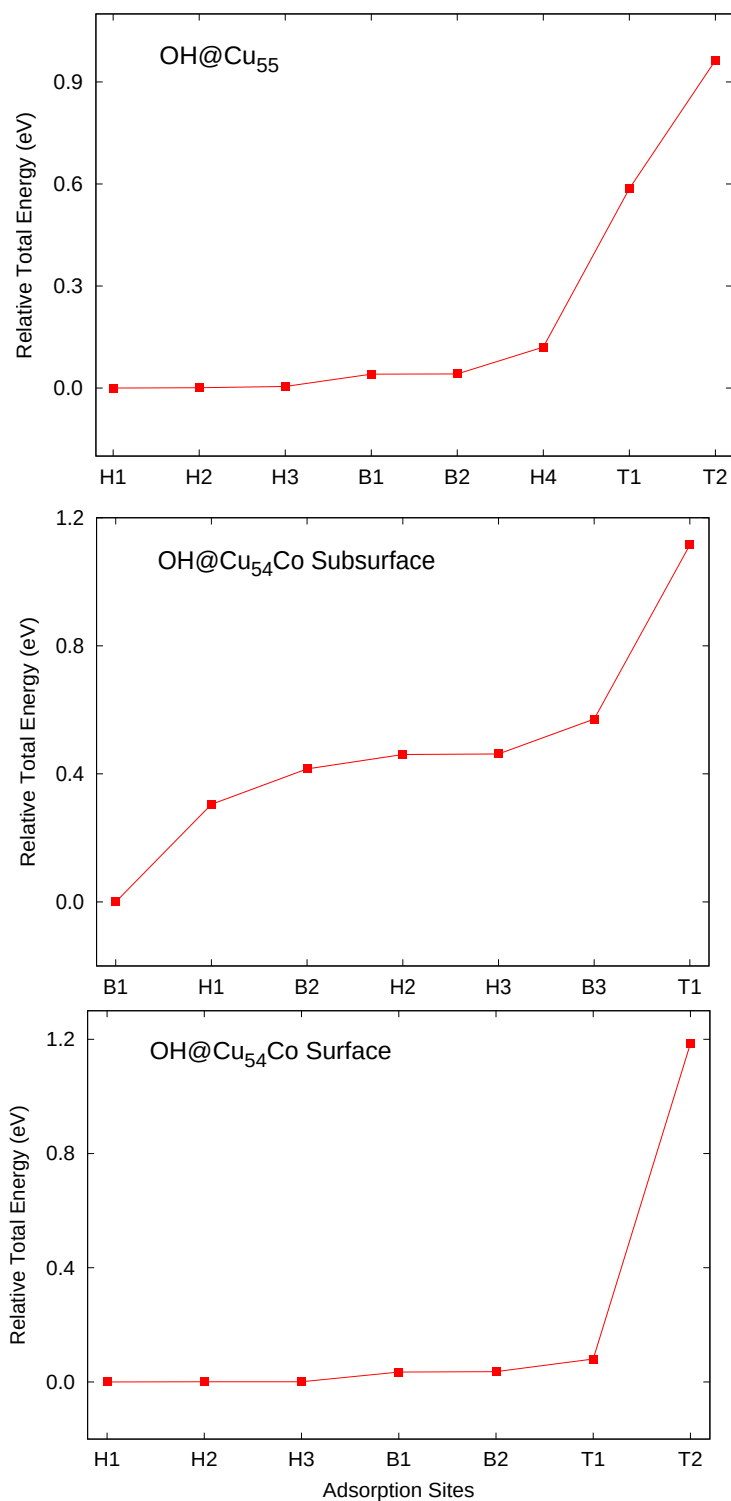


Figure 30 – Relative energies of the optimized OH adsorption configurations on the Cu₅₅ and Cu₅₄Co clusters. The most energetically stable configuration is used as reference.

Figure 31 shows the adsorption sites, geometries and relative energy after optimization for the adsorption of OH on Cu₅₅ nanoclusters. The structures are in ascending order of energy.

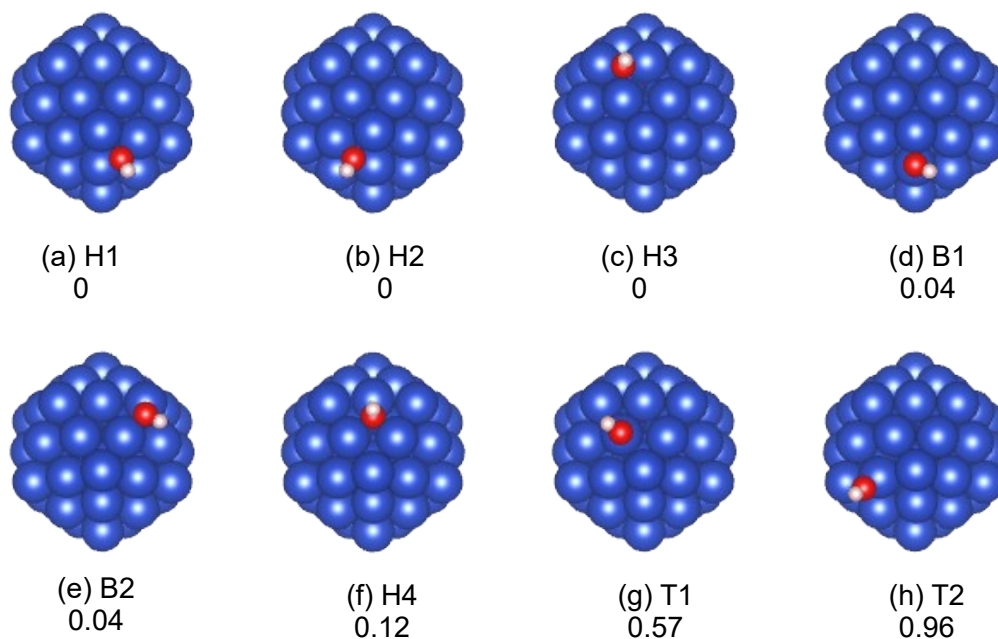


Figure 31 – Optimized configurations (OH@Cu₅₅) after adsorption of OH into Cu₅₅. Adsorption sites and relative energy eV.

Figures 32 and 33 show the adsorption sites, geometries and relative energy after optimization for the adsorption of OH on Cu₅₄Co nanoclusters. The structures are in ascending order of energy.

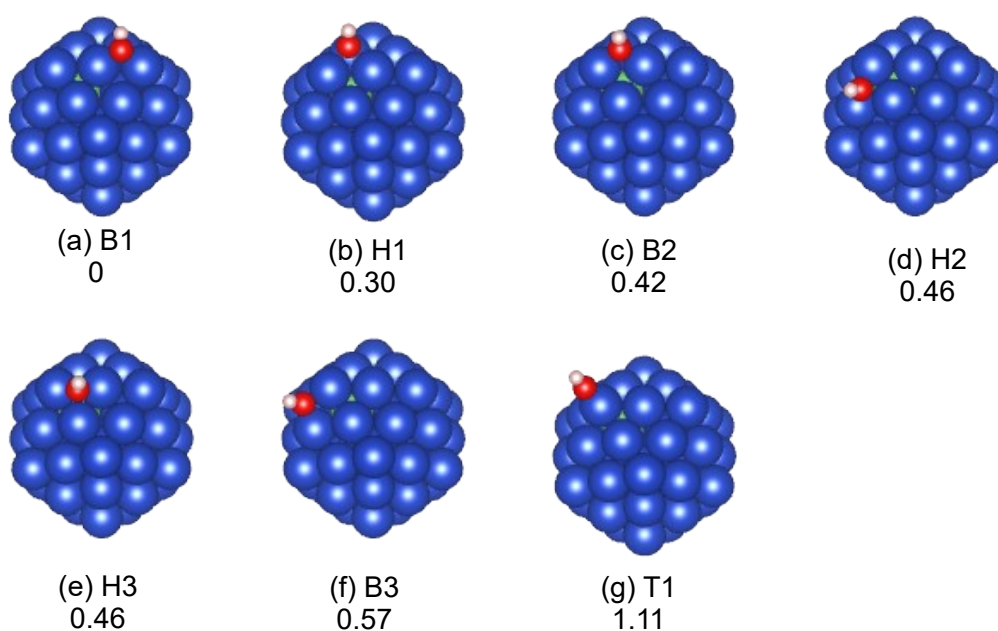


Figure 32 – Lowest energy structures (OH@Cu₅₄Co) upon adsorption on the clusters in the subsurface position. Adsorption sites and relative energy eV

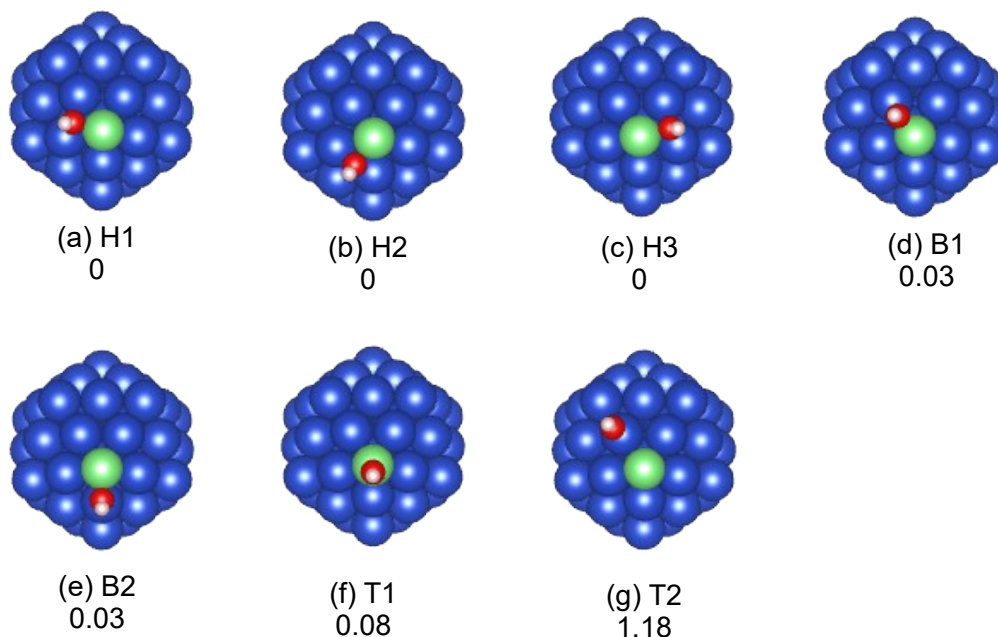


Figure 33 – Lowest energy structures (OH@Cu₅₄Co) upon adsorption on the clusters in the surface position. Adsorption sites and relative energy eV

Figure 34 shows the shortest distance from the oxygen atom to the cluster. The first in relation to the non-doped cluster and the second in relation to the doped cluster.

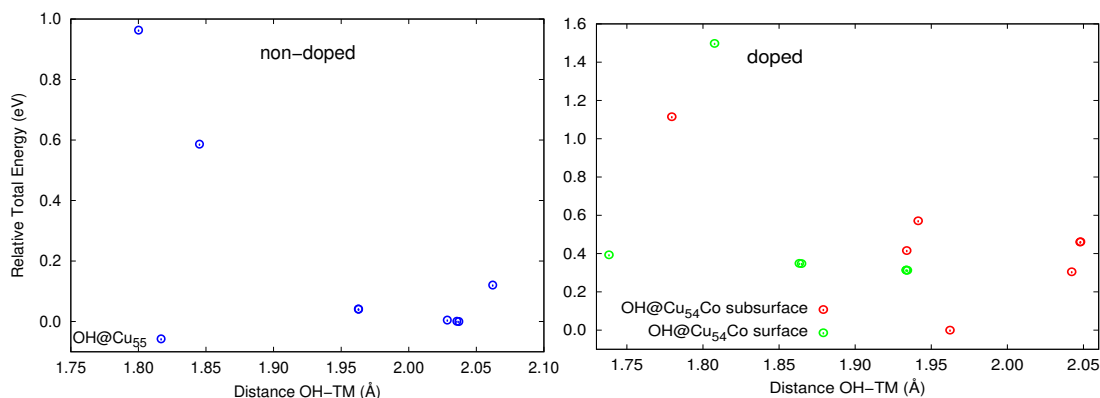


Figure 34 – Relative energies of the adsorbed configurations of an OH molecule over the Cu₅₅ cluster as function of the shortest Cu–O distance.

4.2.5 CO Adsorption

For the CO adsorption, according to Figure 35, when the cluster is non-doped, the most stable configurations are hollow. However when the cluster is doped, all optimizations led to top configurations, even those that started on bridge or hollow configurations. It can be seen that the presence of the cobalt atom, even in the subsurface, drastically change the site preferences.

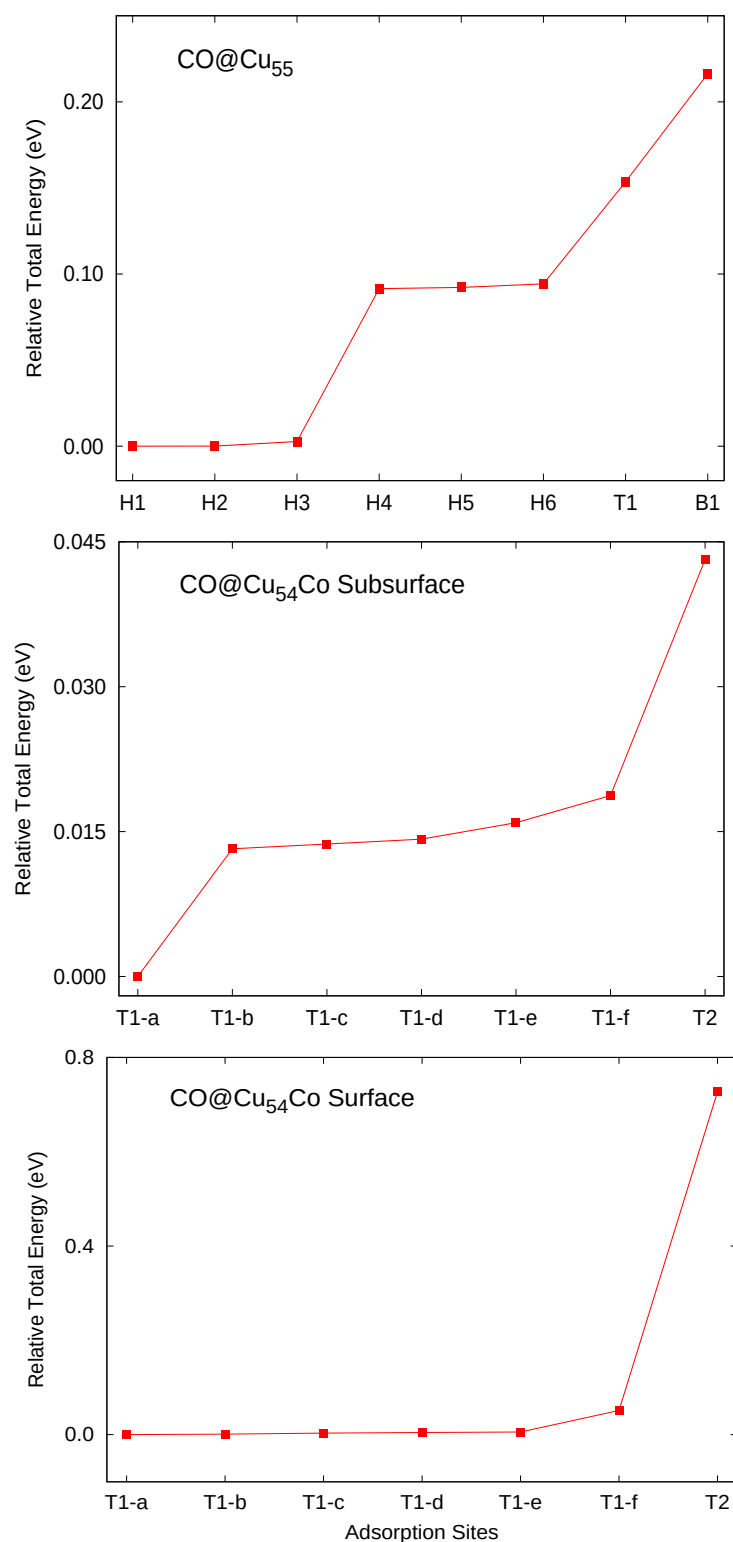


Figure 35 – Relative energies of the optimized CO adsorption configurations on the Cu₅₅ and Cu₅₄Co clusters. The most energetically stable configuration is used as reference.

Figure 36 shows the adsorption sites, geometries and relative energy after optimization for the adsorption of CO on Cu₅₅ nanoclusters. The structures are in ascending order of energy.

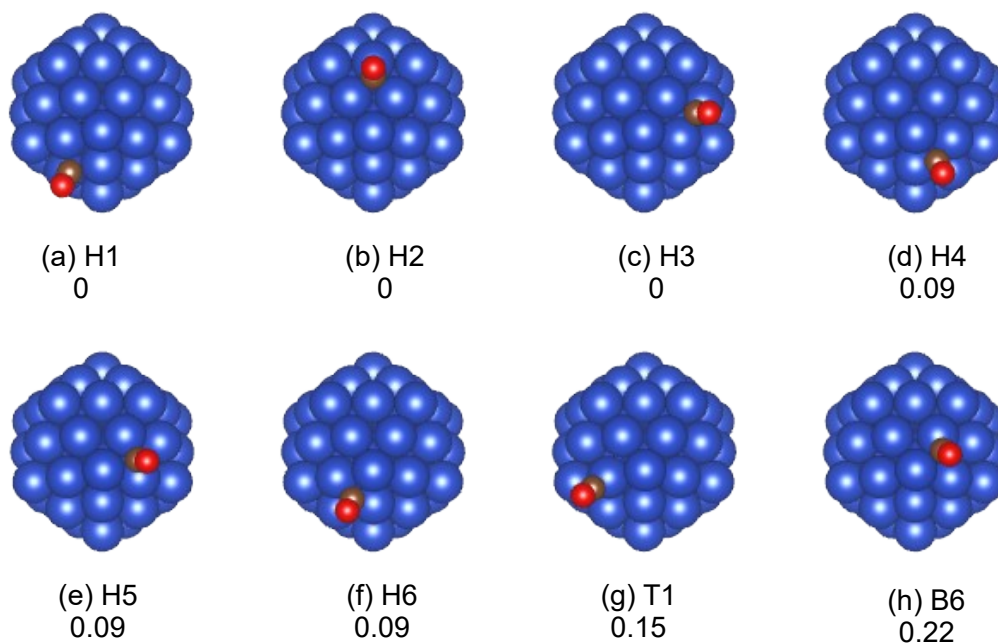


Figure 36 – Optimized configurations (CO@Cu₅₅) after adsorption of CO into Cu₅₅. Adsorption sites and relative energy eV.

Figures 37 and 38 show the adsorption sites, geometries and relative energy after optimization for the adsorption of CO on Cu₅₄Co nanoclusters. The structures are in ascending order of energy.

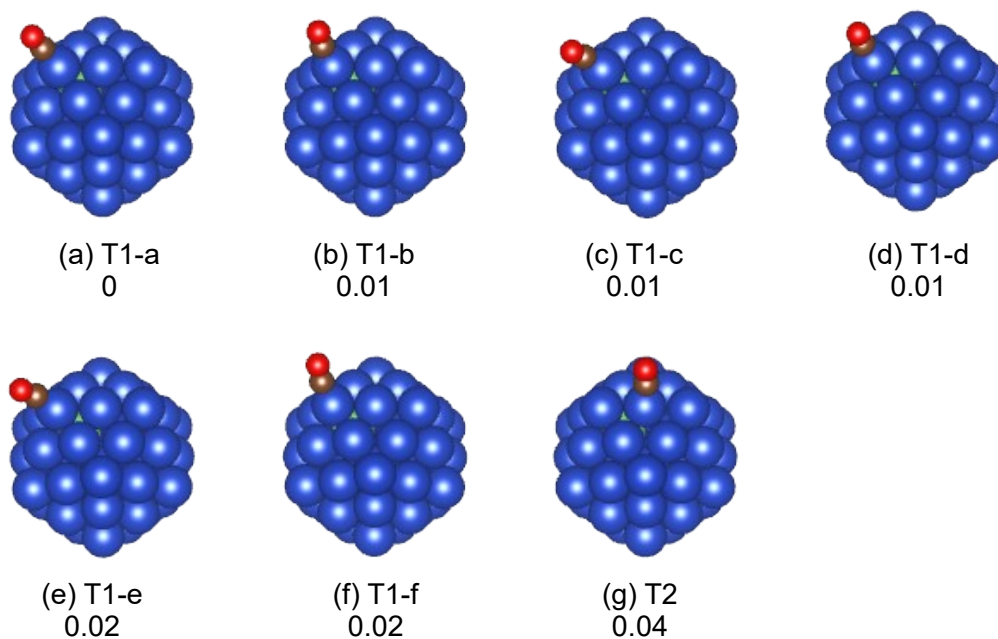


Figure 37 – Lowest energy structures (CO@Cu₅₄Co) upon adsorption on the clusters in the subsurface position. Adsorption sites and relative energy eV.

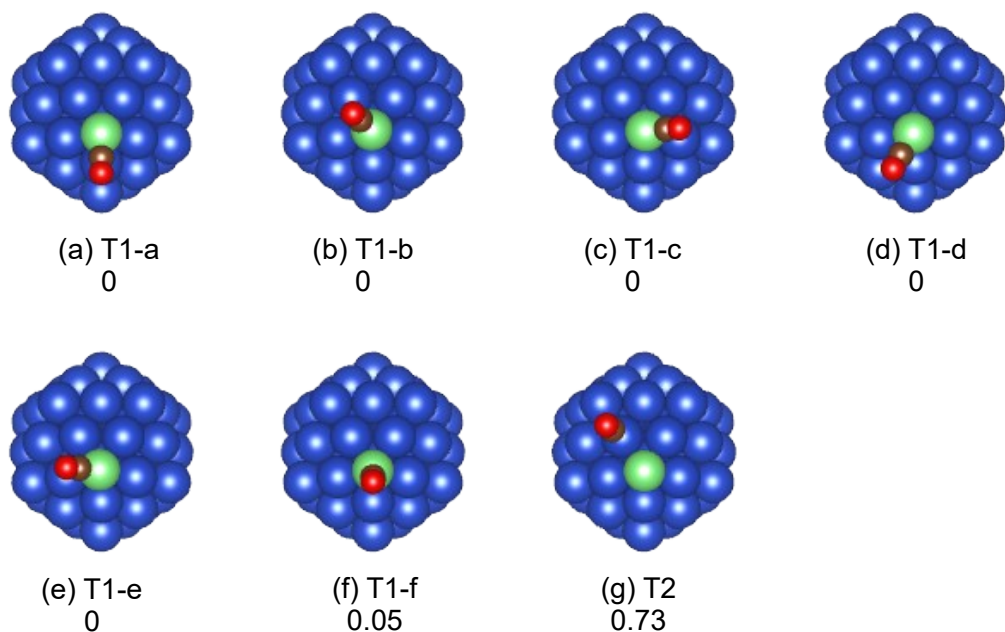


Figure 38 – Lowest energy structures (CO@Cu₅₄Co) upon adsorption on the clusters in the surface position. Adsorption sites and relative energy eV.

Figure 39 shows the shortest distance from the carbon atom to the cluster. The first in relation to the non-doped cluster and the second in relation to the doped cluster. .

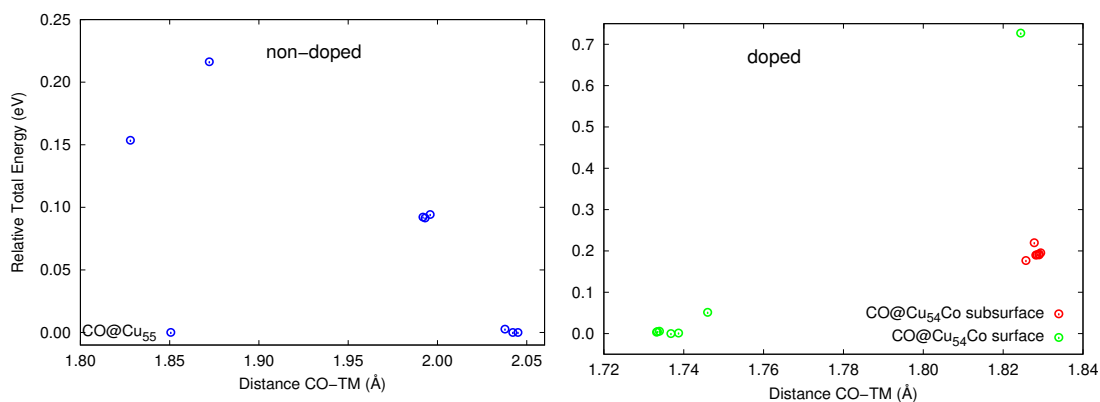


Figure 39 – Relative energies of the adsorbed configurations of an CO molecule over the Cu₅₅ cluster as function of the shortest Cu – C distance.

4.2.6 COH Adsorption

For the COH adsorption, in both situations, that is, non-doped or doped, the most stable configurations are hollow as shown in Figure 40.

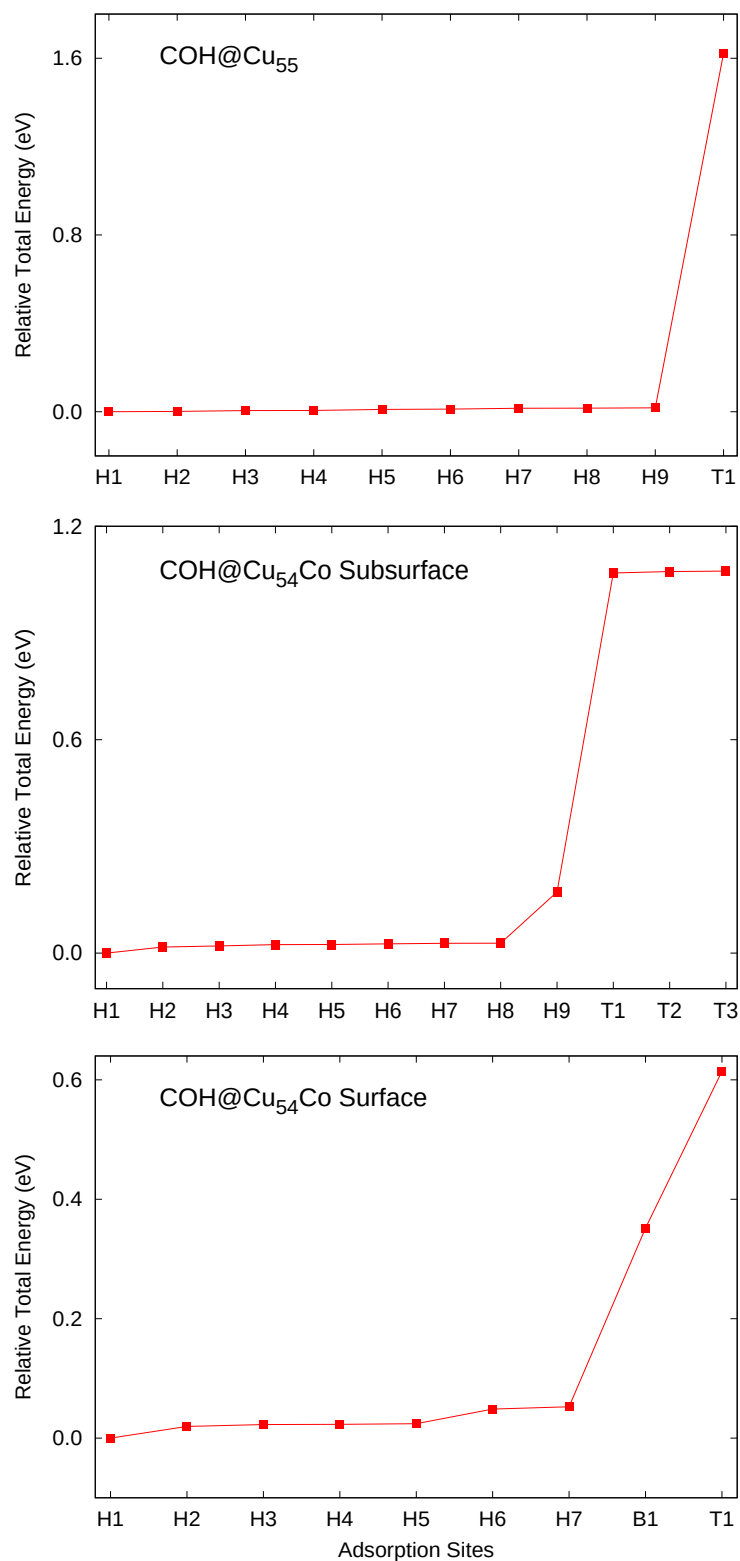


Figure 40 – Relative energies of the optimized COH adsorption configurations on the Cu₅₅ and Cu₅₄Co clusters. The most energetically stable configuration is used as reference.

Figure 41 shows the adsorption sites, geometries and relative energies after optimization for the adsorption of COH on Cu₅₅ nanoclusters. The structures are in ascending order of

energy.

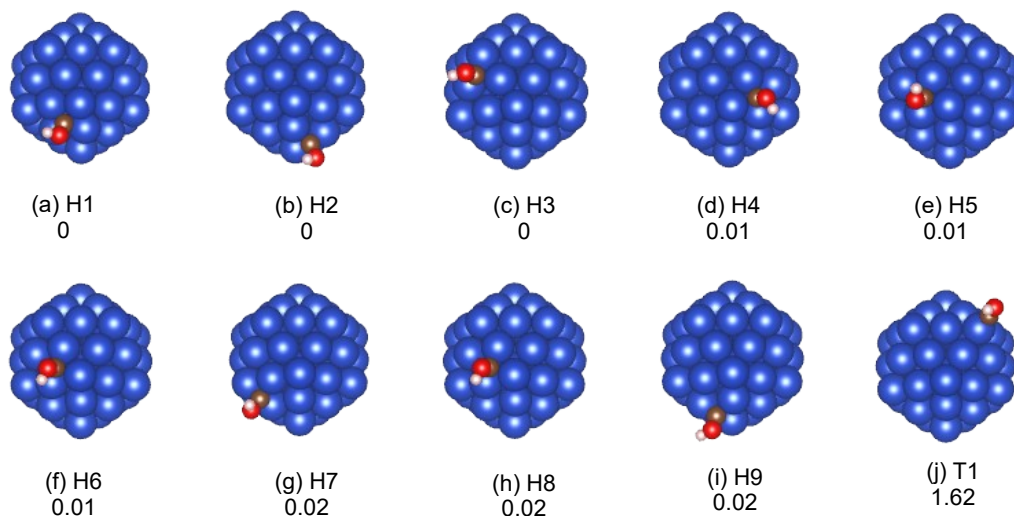


Figure 41 – Optimized configurations (COH@Cu₅₅) after adsorption of COH into Cu₅₅. Adsorption sites and relative energy eV.

Figures 42 and 43 show the adsorption sites, geometries and relative energy after optimization for the adsorption of COH on Cu₅₄Co nanoclusters. The structures are in ascending order of energy.

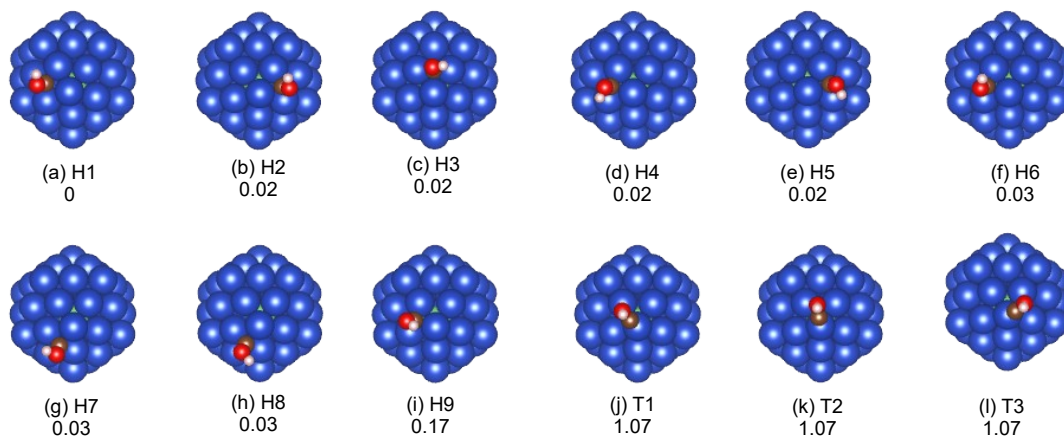


Figure 42 – Lowest energy structures (COH@Cu₅₄Co) upon adsorption on the clusters in the subsurface position. Adsorption sites and relative energy eV.

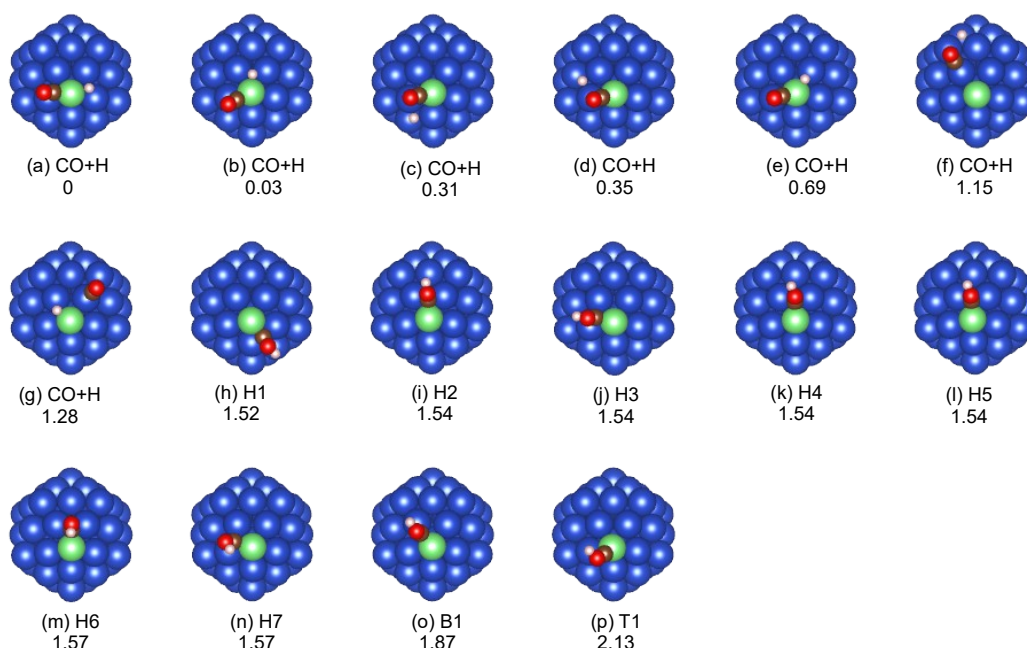


Figure 43 – Lowest energy structures (COH@Cu₅₄Co) upon adsorption on the clusters in the surface position. Adsorption sites and relative energy eV.

Figure 44 shows the shortest distance from the carbon atom to the cluster. The first in relation to the non-doped cluster and the second in relation to the doped cluster. In some cases after the optimization there was breakdown of the chemical bond and the CO molecule ended up bound separately from the hydrogen atom to the cluster and this configuration is the most stable.

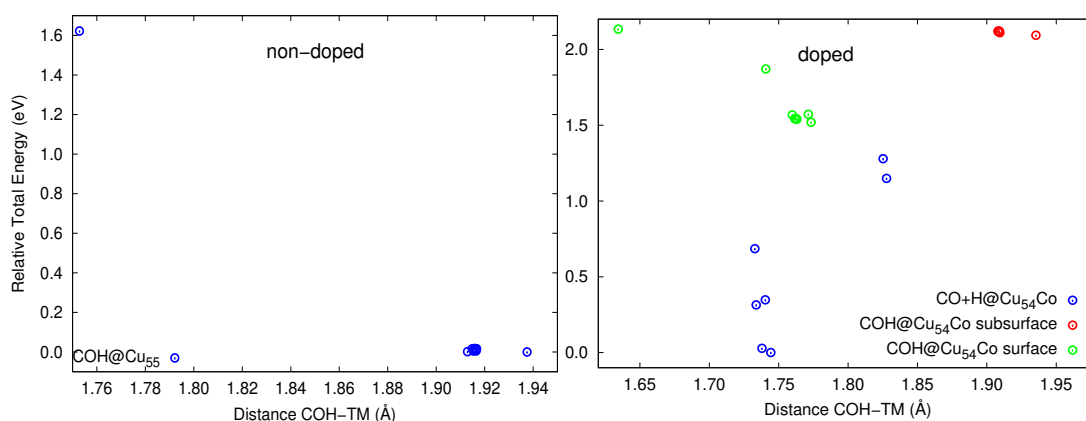


Figure 44 – Relative energies of COH adsorbed on the Cu₅₅ cluster as function of the shortest Cu – C distance.

Figure 53 shows angle formed by the C, O and H atoms of COH molecule after optimization.

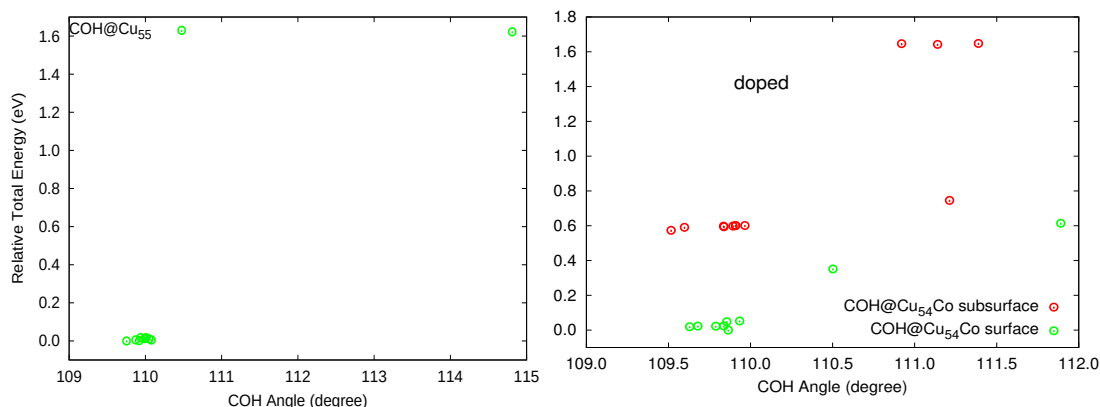


Figure 45 – Relative energies of COH adsorbed on the Cu_{55} cluster as function as a function of the angle formed by C, O and H atoms. In gas phase, using the same calculations parameters the angle formed by C, O and H atoms are 115.5 degrees.

Figure 53 shows C–O distances of COH molecule.

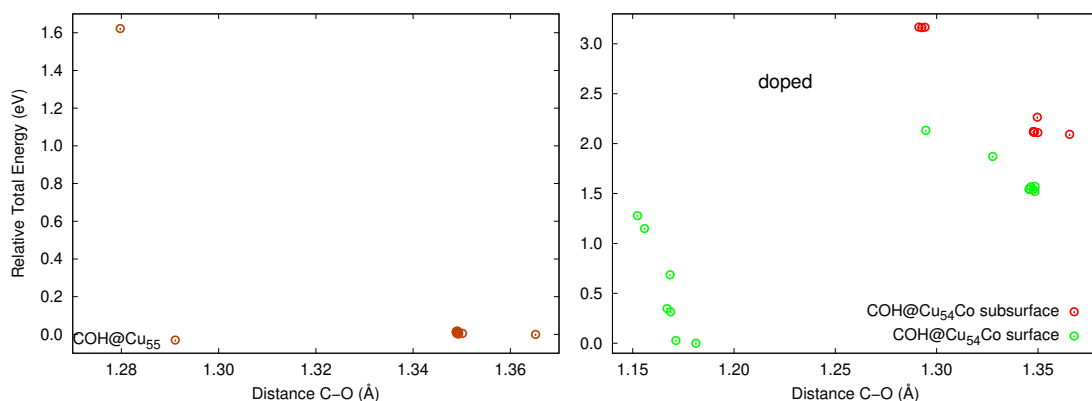


Figure 46 – Relative energies of COH adsorbed on the Cu_{55} cluster as function of the C–O distance. In gas phase, using the same calculations parameters, the distance between C and O of the COH molecule is 1.27 Å.

4.2.7 HCO Adsorption

For the HCO adsorption according to Figure 47, after the optimization the most stable configurations are bridge as when the cluster is non-doped as when it is doped.

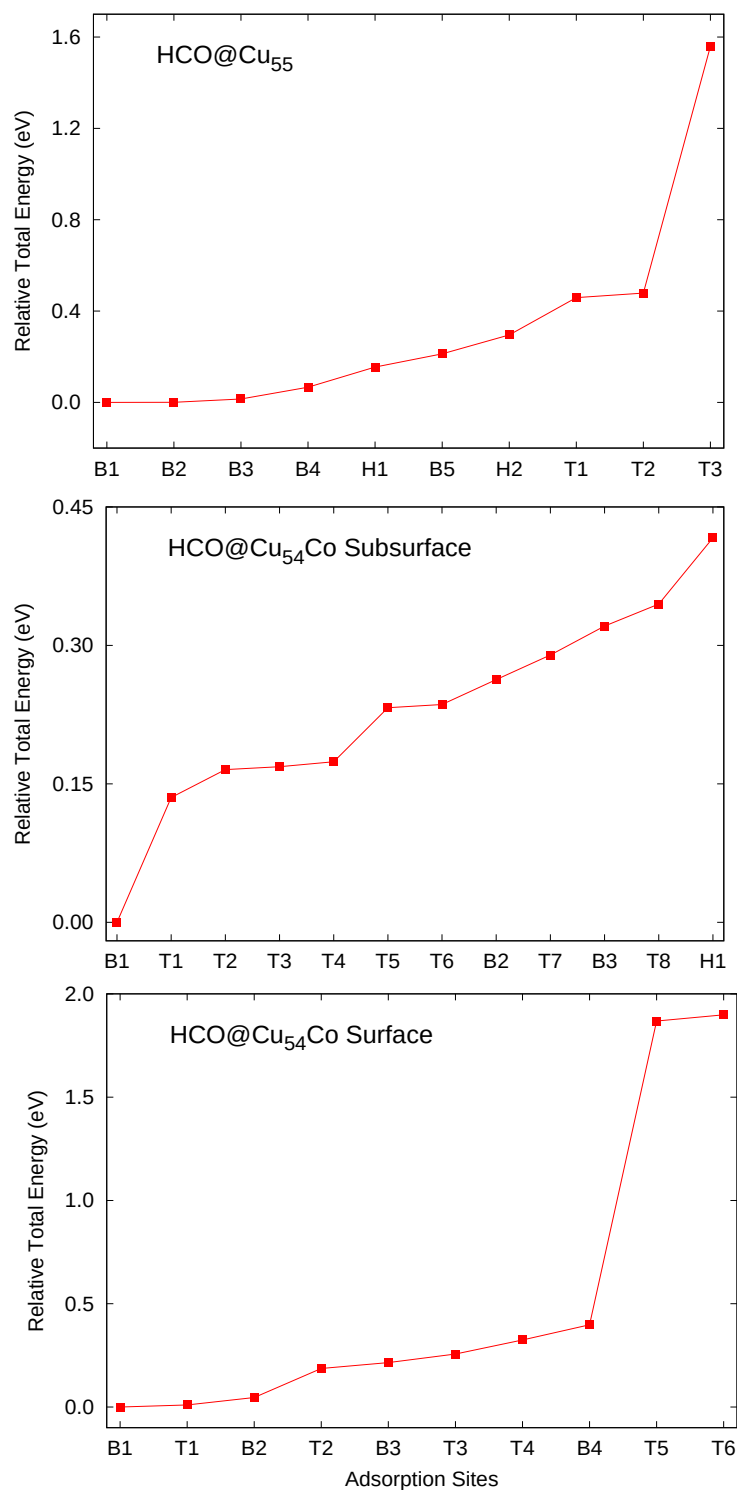


Figure 47 – Relative energies of the optimized HCO adsorption configurations on the Cu₅₅ and Cu₅₄Co clusters. The most energetically stable configuration is used as reference.

Figure 48 shows the adsorption sites, geometries and relative energies after optimization for the adsorption of HCO on Cu₅₅ nanoclusters. The structures are in ascending order of energy.

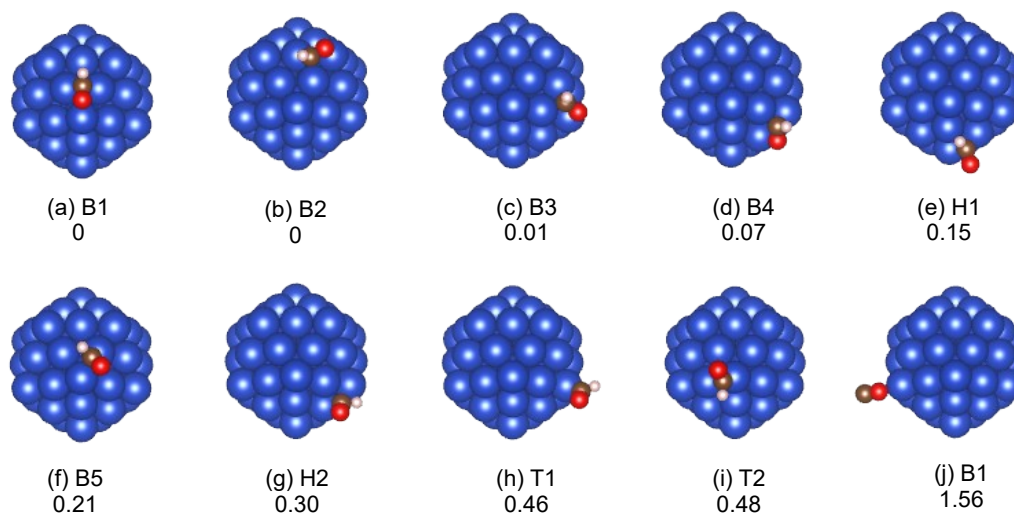


Figure 48 – Optimized configurations (HCO@Cu₅₅) after adsorption of HCO into Cu₅₅. Adsorption sites and relative energy eV.

Figures 49 and 50 show the adsorption sites, geometries and relative energy after optimization for the adsorption of HCO on Cu₅₄Co nanoclusters. The structures are in ascending order of energy.

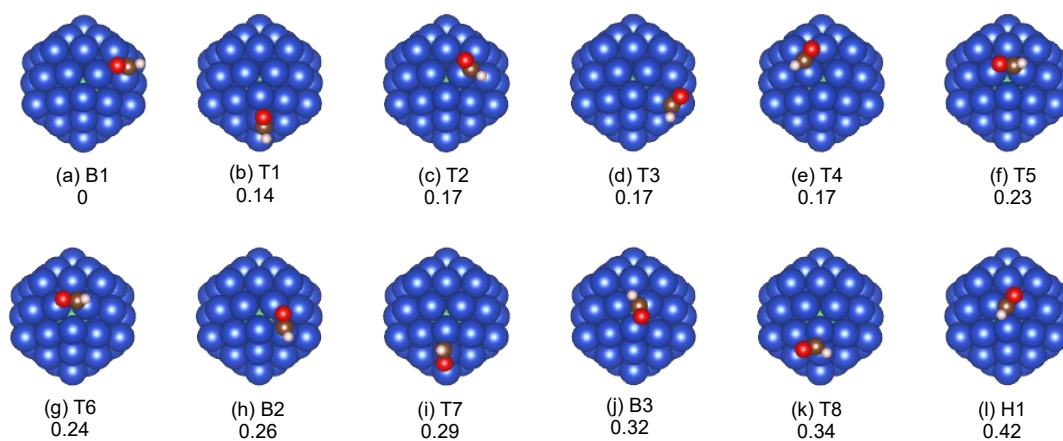


Figure 49 – Lowest energy structures (HCO@Cu₅₄Co) upon adsorption on the clusters in the subsurface position. Adsorption sites and relative energy eV.

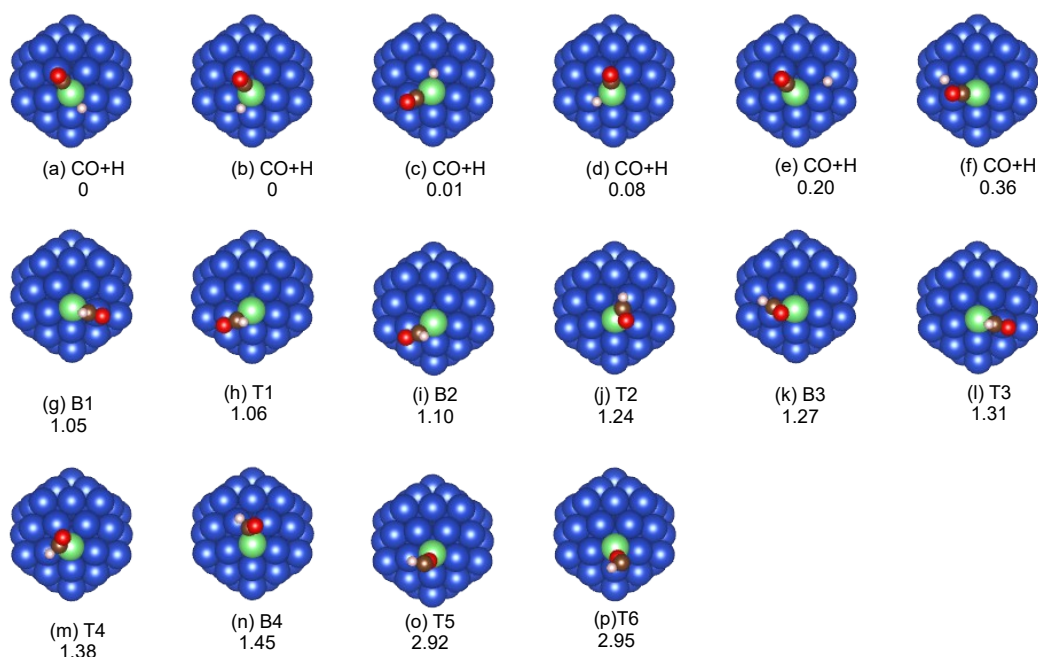


Figure 50 – Lowest energy structures (HCO@Cu₅₄Co) upon adsorption on the clusters in the surface position. Adsorption sites and relative energy eV.

Figure 52 shows the shortest distance from the carbon atom to the cluster. The first in relation to the non-doped cluster and the second in relation to the doped cluster. When the cluster is doped, the same is observed in regard to the break down of the chemical bond, in which the most stable configuration are when this occurs.

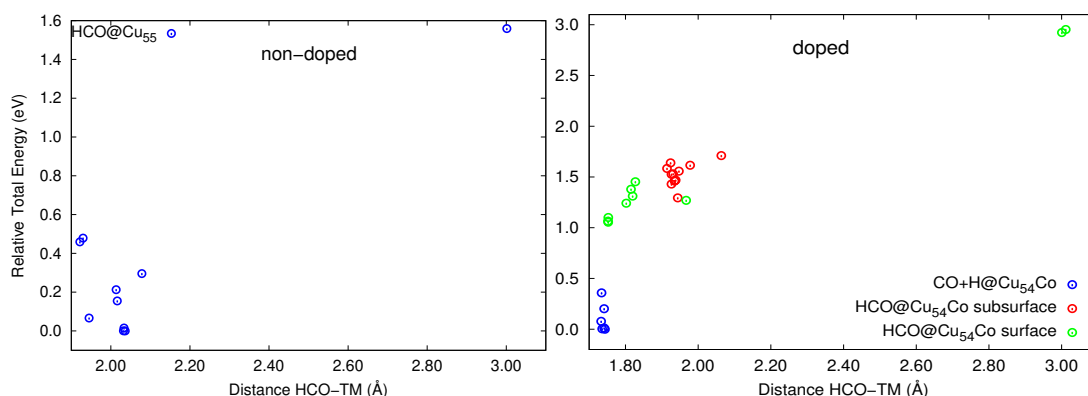


Figure 51 – Relative energies of HCO adsorbed on the Cu₅₅ cluster as function of the shortest Cu – C distance.

Figure 52 shows the angles formed by C, O and H of HCO molecule after optimization.

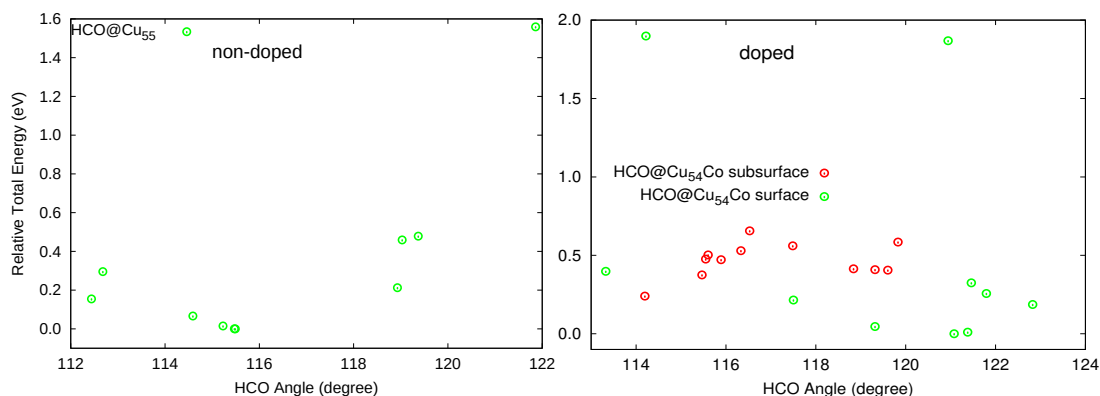


Figure 52 – Relative energies of HCO adsorbed on the Cu_{55} cluster as function as a function of the angle formed by H, C and O atoms. In gas phase, using the same calculations parameters the angle formed by C, O and H atoms are 124.18 degrees.

Figure 53 shows distances C–O of the HCO molecule.

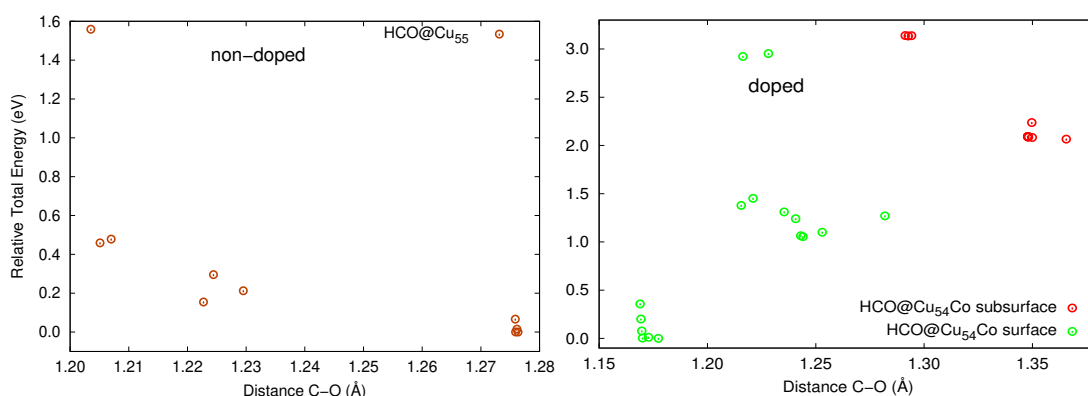


Figure 53 – Relative energies of HCO adsorbed on the Cu_{55} cluster as function of the C–O distance. In gas phase, using the same calculations parameters, the distance between C and O of the HCO molecule is 1.18 Å.

4.2.8 COH and HCO Adsorptions

In order to compare the distances between carbon atoms and the cluster, we present the Figure 54, which shows the absorption of COH and HCO molecules. This graph also shows the distances when the breakdown of chemical bonds occurs and the CO molecule binds separately from the H to the cluster.

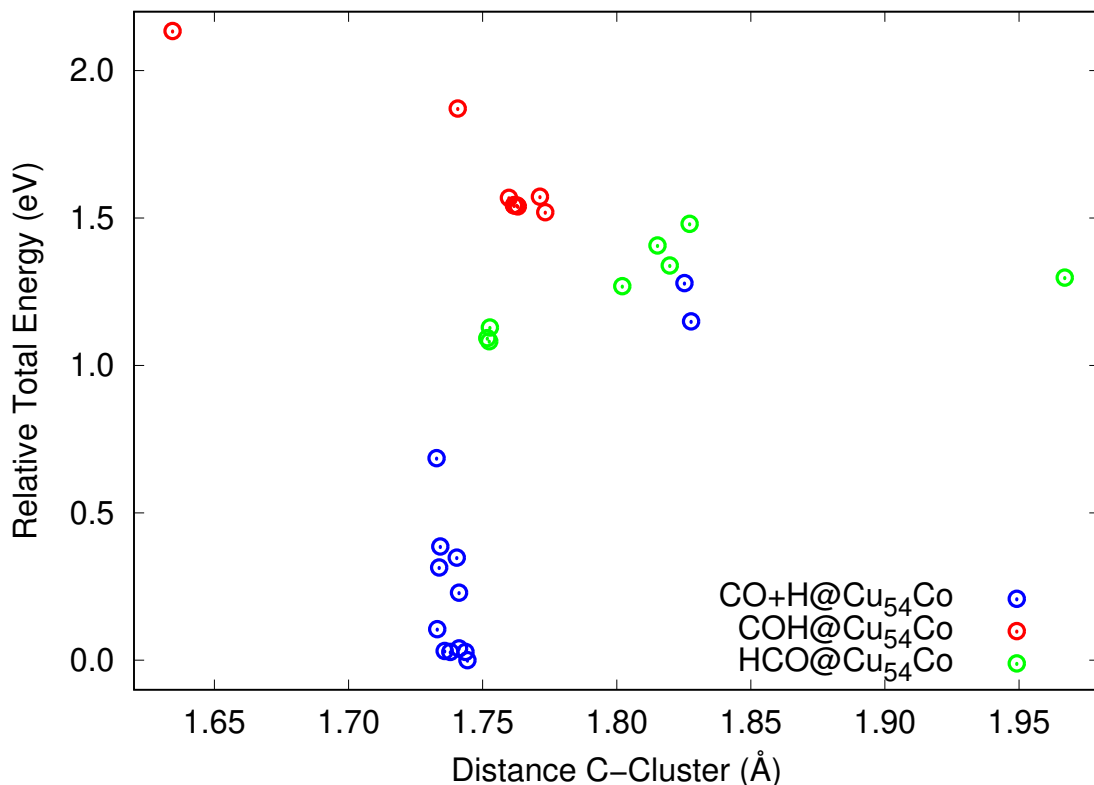


Figure 54 – Relative energies of COH and HCO adsorbed on the Cu₅₅ cluster as function of the shortest Cu – C distance.

4.3 Energetic Contributions from Vibrational Calculations

The computational hydrogen electrode model (*CHE*) (NØRSKOV et al., 2004; PETERSON et al., 2010) was employed to compute free energy changes (ΔG) for the considered electrochemical steps. The free energies are calculated through the equation:

$$G = E_{tot} + ZPE + \int C_p dT - TS + E_{sol} \quad (36)$$

This eq. 36 is the same as discussed in the methodology section (energy analyses). The data referring to the solvation energies were obtained studies (i) proposed by PETERSON et al. labeled like "solvation correction 1"(SC1); (ii) proposed by RENDÓN-CALLE; BUILES; CALLE-VALLEJO labeled like "salvation correction 2"(SC2).

The values obtained in Table 2, regarding the non-adsorbed species, took into account the ideal gas limit, following the approach described by PETERSON et al.. An additional -0.51 eV was added as a gas-phase correction (GPC) to the energy of CO as calculated by PETERSON et al. because of inconsistencies of thermochemical data calculated with the PBE functional.

Molecule	ZPE	$\int C_p dT$	TS	Total	E_{sol}^{SC1}	E_{sol}^{SC2}	GPC
H ₂	0.278	0.091	0.469	0.838	0.00	0.00	
OH	0.223	0.091	0.551	0.865	-0.50	-0.58	
CO	0.132	0.091	0.686	0.909	-0.10	0.00	-0.51
COH	0.328	0.105	0.694	1.127	-0.25	-0.45	
HCO	0.343	0.105	0.694	1.142	-0.10	0.00	

Table 2 – Values of ZPE , $\int C_p dT$, TS and the sum of this quantities, for the gas phase molecules. E_{sol} obtained from the literature, SC1(PETERSON et al., 2010) and SC2.(RENDÓN-CALLE; BUILES; CALLE-VALLEJO, 2020).

System	ZPE	$\int C_p dT$	TS	Total	E_{sol}^{SC1}	E_{sol}^{SC2}
H@Cu ₅₅	0.17	0.004	0.005	0.179	0.00	0.00
OH@Cu ₅₅	0.342	0.05	0.082	0.474	-0.50	-0.58
CO@Cu ₅₅	0.181	0.072	0.132	0.385	-0.10	0.00
COH@Cu ₅₅	0.472	0.075	0.131	0.678	-0.25	-0.45
HCO@Cu ₅₅	0.454	0.074	0.132	0.66	-0.10	0.00

Table 3 – Values of ZPE , $\int C_p dT$, TS and the sum of this quantities, for the molecules adsorbed in unary clusters. E_{sol} obtained from the literature, SC1(PETERSON et al., 2010) and SC2.(RENDÓN-CALLE; BUILES; CALLE-VALLEJO, 2020).

System	ZPE	$\int C_p dT$	TS	Total	E_{sol}^{SC1}	E_{sol}^{SC2}
H@Cu ₅₄ Co	0.164	0.005	0.006	0.175	0.00	0.00
OH@Cu ₅₄ Co	0.351	0.049	0.084	0.484	-0.50	-0.58
CO@Cu ₅₄ Co	0.189	0.055	0.109	0.353	-0.10	0.00
COH@Cu ₅₄ Co	0.47	0.076	0.136	0.682	-0.25	-0.45
HCO@Cu ₅₄ Co	0.461	0.071	0.127	0.659	-0.10	0.00

Table 4 – Values of ZPE , $\int C_p dT$, TS and the sum of this quantities, for the molecules adsorbed in unary clusters doped in the subsurface. E_{sol} obtained from the literature, SC1(PETERSON et al., 2010) and SC2.(RENDÓN-CALLE; BUILES; CALLE-VALLEJO, 2020).

System	ZPE	$\int C_p dT$	TS	Total	E_{sol}^{SC1}	E_{sol}^{SC2}
H@Cu ₅₄ Co	0.216	0.005	0.006	0.227	0.00	0.00
OH@Cu ₅₄ Co	0.342	0.05	0.083	0.475	-0.50	-0.58
CO@Cu ₅₄ Co	0.198	0.071	0.147	0.416	-0.10	0.00
COH@Cu ₅₄ Co	0.474	0.078	0.14	0.692	-0.25	-0.45
HCO@Cu ₅₄ Co	0.42	0.064	0.126	0.61	-0.10	0.00

Table 5 – Values of ZPE , $\int C_p dT$, TS and the sum of this quantities, for the molecules adsorbed in unary clusters doped in the surface. E_{sol} obtained from the literature, SC1(PETERSON et al., 2010) and SC2.(RENDÓN-CALLE; BUILES; CALLE-VALLEJO, 2020).

Gibbs energy is a very important thermodynamical property that predicts the spontaneity of a chemical reaction. In figure 55 we show the free energy diagrams for CO₂ reduction towards COH and HCO. Two results are presented, comparing the different values of solvation energy.

CO adsorption in the gas phase is favorable due to the decrease in the ΔG value, however the COH and HCO formation requires more energy, thus proving to be an unfavorable process.

In relation to COH and HCO formation, we can see that HCO formation is more favorable because of small energy variation of the transition step from CO to HCO when compared to COH. Take into account the doping, when the cluster is non-doped and doped in the subsurface for both cases, we can conclude that there were no major variations, however when the doping is made in the surface, the formation of products is more favorable.

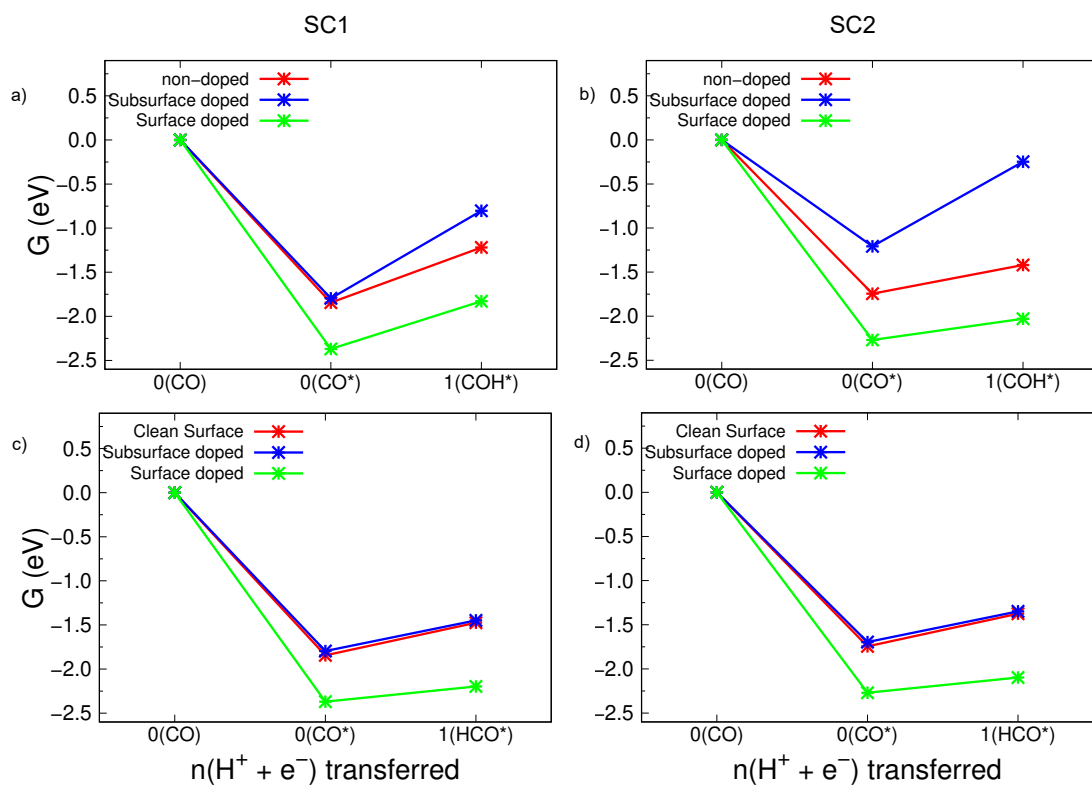


Figure 55 – Free energy diagrams for CO_2 reduction towards COH (a and b) and HCO (c and d). For comparison, we show the results obtained with solvation energies obtained through the two methods reported in this work (SC1 and SC2).

Chapter 5

Conclusions

Adsorption is a crucial stage of the catalysis process, being the essential first step, therefore understanding this process is important to development of new catalysts. In this work we present a discussion about the intermediates (H, OH, CO, COH and HCO) adsorption of CO₂RR with intention to comprehend how this phenomenon occurs in copper nanoclusters. We also verify the doping effect to the cluster by replacing a copper atom by a cobalt atom.

Icosahedral structures are the most stable configurations for the nanoclusters studied. From this configuration it was possible to study the cobalt doping and conclude that the most stable configurations are when the cobalt atom is replaced in the core. However, in order to investigate the doping effect in the surface, a configuration with cobalt atom in the surface was chosen to compare the results. The effective coordination number (ECN) was an important tool because it was possible to map the non-equivalent atoms in an icosahedron configuration since this approach can be applied for symmetric or distorted structures consistently.

In this work, we employed a screening strategy in a first stage. This approach was important, because there is a large number of possibilities spatial arrangements and adsorption sites, resulting in a large quantity of calculations. As such, the reduction of resources and computational time enabled one to have an idea about the preferential adsorption sites, thus to obtain the final results.

Through calculations using DFT, it was possible to study the interactions between the intermediates of CO₂RR with copper nanoclusters and to conclude that, the adsorbates concerned have preference in hollow sites to adsorb, except HCO, which tends to be most stable in bridge sites. In relation to the doping of the cluster with cobalt, primarily taking into consideration the doping in the subsurface, we show the results are the same as those obtained when the cluster was non-doped, but OH and CO were most stable in bridge and top sites respectively. When we doped the cluster in the surface, we verify the same trend

observed previously, when the cluster was non-doped, except for CO adsorption, which presented the lowest energies in top sites. So we conclude that the doping mainly affected the CO and OH adsorptions. In relation to COH and HCO adsorptions, we can conclude which they are less stable than broken $\text{H}+\text{CO}$ configurations.

From the results obtained, using the most stable systems, we performed calculations employing the computational hydrogen electrode model to compute free energy changes for the considered electrochemical steps, and we conclude that CO adsorption is favorable, however the COH and HCO formation requires more energy. COH is more difficult to form when compared to HCO and the doping shows major differences when it is made in the surface.

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