

Phosphorus doping of carbon-based materials for single atom catalysis

BACHELOR THESIS

Andrea Ruiz Ferrando

Academic director: Dra. Mar Reguero Professional director: Prof. Núria López Supervisor: Edvin Fako Chemistry degree 2018/2019

CONTENTS

Abstract	2
Objectives	3
Introduction	4
Theoretical Background	7
d-band theory: metal – non-metal interaction approach	7
Density Functional Theory and Periodic Boundary Conditions	8
Methods	13
Results and discussion	18
Conclusions	33
References	35

ABSTRACT

p-block-doping has been used as a powerful tool to tune electronic properties of carbon-based materials for a great variety of applications. However, phosphorus doped carbons are poorly explored, particularly as single-atom-catalyst scaffolds. In this work, Density Functional Theory is employed to compare different phosphorus-doped carbon-based materials as supports for single atom catalysis. Computed X-ray Photoelectron Spectroscopy shifts are presented and show the possibility of chemically different P or Pd atoms exhibiting similar shifts. The potential activity of P-doped-carbon supported Pd single atoms has been discussed in terms of the Projected Density of States. This work demonstrates the viability of some phosphorus-doped carbon-based materials to be used as single atom scaffolds and opens up the possibility of bridging homogeneous and heterogeneous catalysis to improve catalytic performance.

RESUM

El dopatge utilitzant elements del bloc p ha estat sovint emprat com a eina per a modificar les propietats electròniques dels materials basats en carboni per a un ampli ventall d'aplicacions. Tot i així, el dopatge amb fósfor ha estat poc explotat, sobretot en suports per a catalitzadors tipus "single atom". En aquest treball, s'empra la Teoria del Funcional de la Densitat per a comparar diferents materials de carboni dopats amb fósfor com a suports per a catàlisi tipus "single atom". Els resultats dels càlculs realitzats sobre espectroscòpia de fotoelectrons emesos per raigs X (XPS) pels àtoms de P i Pd de les estructures demostren possibles diferents entorns químics del fósfor i el pal·ladi amb mateix desplaçament XPS. L'activitat catalítica dels catalitzadors de Pd "single atom" suportats sobre els suports dopats ha estat predita per mitjà de l'anàlisi de l'estructura electrònica a través del càlcul de densitat d'estats. Aquest treball demostra la viabilitat d'obtenció dels materials estudiats per a ser emprats com a suports i suggereix la possibilitat d'unir la catàlisi homogènia i l'heterogènia per tal de millorar l'activitat catalítica.

OBJECTIVES

The main objective of this work is to compare different phosphorus-doped carbon-based materials to identify the most promising candidates for being used as single atom catalyst supports.

Two sets of materials are studied. On the one hand, P-doped graphene and their palladiumderived systems are investigated, as scaffolds with new coordination sites created from pristine graphene. On the other hand, P-doped $g-C_3N_4$ and their Pd corresponding systems, as supports with modified already-existing coordination sites.

By using DFT, the aim of this study is to evaluate the viability of obtaining these materials and predict their catalytic performance. Besides this, these computational investigations are also carried out in order to evaluate phosphorus doping effects in the electronic structure of these materials to assess their catalytic behavior.

OBJECTIUS

El principal objectiu d'aquest treball és comparar diferents materials de carboni dopats amb fósfor per a ser emprats com a suports per a catalitzadors tipus "single atom" per tal d'identificar els més prometedors.

Es volen estudiar dos grups de materials: suports basats en grafè i en nitrur de carboni, així com els corresponents catalitzadors de pal·ladi tipus "single atom" que en deriven. Els suports derivats de grafè es volen estudiar com a sistemes on s'han generat nous llocs de coordinació, mentre que els que s'obtenen a partir de nitrur de carboni es tracten com a modificació de llocs de coordinació prèviament existents.

Per mitjà de DFT, la finalitat de l'estudi és evaluar la viabilitat d'obtenció d'aquests materials i predir la seva activitat catalítica. A més, les investigacions computacionals realitzades pretenen comprendre l'efecte del dopatge amb fósfor en l'estructura electrònica d'aquests materials per tal de poder evaluar el seu comportament catalític.

INTRODUCTION

This work has been developed in Institut Català d'Investigació Química (ICIQ) in Tarragona, in Prof. Núria López' group, in Theoretical and Computational Chemistry. It has been directed by Prof. Núria López and co-directed by Edvin Fako.

The field of Catalysis is in need of a revolution due to the need of reducing the impact of the industry on the environment.^[1] Specifically, industrial catalysis is the key factor allowing for sustainable chemistry both in terms of economic and ecological justifications. Catalysts, according to their most general definition provide alternative, more kinetically favourable routes of executing chemical reactions, and in that way reduce waste, either by side-products, or indirectly, by avoiding harsh conditions necessary for non-catalysed reactions. Particularly heterogeneous catalysts help in reducing solvent consuming (for extractions, separations, etc.) which simplifies chemical technological processes.^[2] Current state-of-the art catalysts are mostly comprised of noble metals and as they are scarce, the downsizing catalyst nanoparticles to single atoms is highly desirable.^[3]

In homogeneous catalysis, catalysts are in the same phase as reactants and products. The activity of such systems is typically high due to efficient catalyst dispersion. Homogeneous catalysts currently provide generally better selectivity as the tools for characterizing and modifying them have been present for nearly a century. Using these tools (organic chemistry techniques, NMR, IR and other spectral methods) allows for the easier tuning of active sites. However, industrial application of homogeneous catalysts is limited because of the difficulty of separating the catalyst from the other species. Heterogeneous catalysts are quite stable and easy to separate, and therefore more practical in industrial applications, but in some cases suffer from inadequate activity and selectivity. There is an emerging catalytic trend that could bridge both types of catalysis and improve the catalytic performance whilst reducing metal loading: singleatom catalysis. Single-atom heterogeneous catalysts (SAHCs) have localized active sites comprised of a single (typically) d-block metal atom, stabilized in its coordination environment. The coordination environment plays a key role in stabilizing the single atom and facilitating its chemical activity acting in a role equivalent to a ligand in homogeneous catalysis. Unlike nanoparticle-based catalysts, their size distribution is sharp, and as individual atoms constitute active sites, they exhibit an optimal catalytic performance: high selectivity, catalytic activity and atomic efficiency. In terms of mechanistic behaviour, the coordination environment of the single atoms governs its activity similarly to homogeneous catalysts, and they can be thought of as lowcoordinated species that are anchored to a support.^{[4][5][6]}

An alternative way of thinking about SAHCs is to imagine reducing the metal nanoparticle size to its absolute limit. Reducing particle size typically leads to strong increases in the free surface energy, and non-linear size/stability correlation for small clusters.^[7] Due to this and to the fact that single atoms on heterogeneous substrates are notoriously difficult to characterize^[8] SAHCs are in early stages of development. For these reasons these catalysts need to be dispersed onto high-surface-area supports that ensure strong interaction with the single atoms to prevent from its sintering.^[3] The electronic structure of supports can modulate the catalytic behaviour of the single atoms anchored on it, and some inert support surfaces can also be activated by single atoms.^[9]

One type of very common SAHC supports are carbon-based 2D materials, such as graphene, for its high elemental abundance and diverse bonding ability of carbon atoms. Graphene is a singleatom layer of sp² hybridized carbon. Such special planar structure provides it with unique properties that makes it excellent for various catalytic processes. Its single atom layer makes it easily tuneable. Besides this, it has excellent physical and chemical properties to act as a catalyst in a lot of processes.^[3] Alike other 2D structures, graphene-based SAHC supports tend to be unique scaffolds in catalysis because they enable single atoms to be exposed directly on the surface as active sites or embedded inside the 2D structure and then modulate the electronic property of the coordination environment in the material. The open structure of 2D materials facilitates mass-transfer processes and ensures 100% exposure of single atoms to reactants. Furthermore, they are ideal model catalysts for understanding the real active site and surface reaction mechanism.^[10]

Other 2D materials have been also used, such as graphitic carbon nitride (g-C₃N₄), which is based on heptazine units bonded by amine groups. It has demonstrated high stability and it is composed of earth-abundant elements.^[11] It has been used as a photocatalytic material for CO₂ reduction, water splitting and pollutant degradation.^[12] Various metals, including Pd, Pt, Ir and Ag, have been successfully stabilised as single atoms on this support.^[11] Like graphene, its large surface area enhances the exposure of its active sites and its photocatalytic potential, but it has larger Ncoordinating cavities than conventional N-doped graphene. Its morphology can be manipulated to even increase its surface area.

The intrinsically high content of six-fold cavities between heptazine units in the N/C-coordinated framework atoms can provide an ideal geometry for metal coordination and even offer possibilities

to be used as semi-conducting photocatalysts.^[1] However, both graphene and $g-C_3N_4$ have presented several drawbacks in its electronic properties that have led to low solar energy conversion in some photocatalytic applications.^[13] To solve this, heteroatom doping has been used as an effective strategy to modify surface and chemical properties, as well as electronic structure. This has led to enhanced electrocatalytic activity.^[14] ^[15] In particular, phosphorus doping has been used several times lately motivated by the desire to mimic P-N heterocyclic ring motifs present in a lot of molecules in nature. Incorporation of P can greatly change electronic properties of $g-C_3N_4$, as it has one more electron than carbon, and its potential substitution to carbon can create an electron-rich state of the material. However, localizing phosphorus precisely in the doped material is still difficult.^[16]

Pd catalysts have been extensively used in a great variety of fields, specially C-C coupling reactions. Pd-(II) salts or complexes, generated in situ by the addition of a ligand are the most common sources of Pd for these chemical processes. These compounds are then reduced to palladium (0) to enter the catalytic cycle.^[17] More recently, some heterogeneous catalytic systems have been developed for these reactions. Pd nanoparticles have been used, in where the reaction takes place in the metal surface or at the defects of the nanoparticles.^[18] Pd-SAHCs have shown to provide a viable way to improve catalytic performance of all these reactions. Despite some theoretical studies have been done with pristine g-C₃N₄ as a Pd single atom support^[19], g-C₃N₄ doping is relatively unexplored.

New materials need to be developed for being used as single atom scaffolds. For this reason, rationalization on materials design is needed. Computational research can provide information to explore new materials and allows to have some data that cannot be obtained experimentally. In fact, modern Chemistry strongly depends on the advances made by Theoretical and Computational Chemistry. The analysis of reaction networks, activity and selectivity issues and the final tests on the stability of the potential materials are fundamental to establish a solid background to determine when a material can be considered as a catalyst candidate for a given chemical transformation. Besides this, the theoretical study of electronic properties to rationalize catalytic behaviour of materials is a useful tool to predict and understand the performance of a particular material.

In this case, computational research is employed to evaluate the viability of the obtaining of a group of materials and predict its potential catalytic performance. Doping of different structures is used as a generation of new anchoring sites. From the one hand, by post-functionalizing

graphene, new coordinative sites can be created in places where they did not exist and from the other hand, modification of carbon nitride can lead to the creation of new coordinative environments in already-existing sites.

THEORETICAL BACKGROUND

d-band theory: metal – non-metal interaction approach

Interactions between adsorbed metal particles and their support must be studied in order to evaluate both the viability of the material and its potential catalytic applications. This holds true even if the particle consists of a single atom (i.e. SAHC), or it describes the interaction between the catalyst and substrate. This interaction can be explained through the examination of the electronic structure of both the non-metal atoms and palladium.

d-band theory, described by Nørskov and co-workers can be applied here.^[20] Despite the fact that this theory refers to metal surfaces and atomic or molecular adsorbates, here it will be applied to a non-metal surface and single metal atoms, with some peculiarities.

In a solid, in contrast to discrete molecules, a very large number of levels and states are present. Therefore, while for a molecule one can consider one orbital or a small sub-group of orbitals to rationalize some behavior, one has to deal with groups of states in a particular energy interval when examining solids. There is no sense in studying one particular orbital or level to influence reactivity of a solid.

Instead of this, density of states can be estimated. It is defined as the number of states in a given interval between E and E + dE. The study of this property can help rationalize conductivity, bonding, etc.^[21]

Metals are characterized by a broad *s* band that is half filled and much narrower *d* bands. The occupancy of the *d* bands depends on the particular metal. The states of an atom or molecule interact with the valence states of the metal, but in a very different way with the *s* and *p* electrons or *d* electrons. *sp* interaction gives rise to completely filled states because they are below the Fermi level, which is the highest occupied level at 0K. However, the interaction of the non-metal states with the *d* bands, as *d* bands are narrow, often leads to bonding and antibonding states just as in a typical two-state problem. This different interaction is shown in **Figure 1**. Since these

antibonding states are above the Fermi level, they are empty. Thus, the bond becomes increasingly stronger as the number of empty antibonding states increases. Therefore, although we can think of the binding energy having two components (one from coupling to *s* electrons and one to the *d* states), the problem can be simplified considering only the *d* band center. As the strongest interaction comes from the *d* states, and this can be considered a two-level problem that leads to a bonding and antibonding states, *d*-band center can be used as a reactivity descriptor. As *d* band center moves up in energy, more antibonding metal – non-metal *d* states become empty, because they are above the Fermi level. Therefore, adsorption becomes more favorable. This relationship allows to use *d* band center here both to assess anchoring ability to the support and potential adsorption of substrates.^[20]



Figure 1. Schematic illustration of the change in local electronic structure as a result of the different interactions in *sp* coupling and *d* coupling.^[20] Taken from: Hammer, B.; Nørskov, J. K. Theoretical Surface Science and Catalysis - Calculations and Concepts. *Adv. Catal.* **45**, 71-129 (2000).

Density Functional Theory and Periodic Boundary Conditions

Theoretical and Computational Chemistry are based on quantum mechanics principles. Quantum mechanics allows the description of the properties of a particular collection of atoms. A key observation is that atomic nuclei are more massive than electrons, so electrons respond much rapidly than nuclei. Therefore, the nuclei can be considered to be in static positions. For this reason, they can be mathematically separated within the Born-Oppenheimer approximation. It allows expressing the ground-state energy as a function of the positions of the nuclei. Considering this approximation, the time-independent, nonrelativistic Schrödinger equation $\hat{H}\varphi = E\varphi$ can be expressed as in **Equation 1**:

$$\left[\frac{h^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}V(r_i) + \sum_{i=1}^{N}\sum_{j Equation 1$$

The three terms define the kinetic energy of each electron, the interaction energy between each electron and the collection of atomic nuclei and the interaction between electrons, respectively. This last term is the most critical part in solving the equation. The individual electron wave function ψ cannot be found without simultaneously considering the individual electron wave functions associated with all the other electrons. Therefore, Schrödinger equation is a many-body problem.

Density functional theory can be developed on two fundamental theorems. The first one, proved by Hohenberg and Kohn is: *The ground-state energy from Schrödinger's equation is a unique functional of the electron density.* This means that the ground-state electron density determines all properties of the ground-state, so that one electron-density corresponds to an energy value. Relating energy and electron density in this terms allows to reduce the dimensionality of the problem.

This theorem does not say anything about the functional, but in the second theorem an important functional feature is described: *The electron density that minimizes the energy of the overall functional is the true density corresponding to the full solution of the Schrödinger equation.* This means that if functional form was known, electron density could be varied until the energy was minimized.

A useful way to write down the functional described by the Hohenberg-Kohn theorem is in terms of the single-electron wave functions. Kohn and Sham developed the task and wrote single-electron equations to find the minimum energy solutions of the total energy functional. The form of these is written in **Equation 2**.

$$\left[\frac{h^2}{2m}\nabla^2 + V(r) + V_H(r) + V_{XC}(r)\right]\psi_i(r) = \varepsilon_i\psi_i(r)$$
 Equation 2

The terms represent, in order, the electron kinetic energies, the Coulomb interactions between the electrons and the nuclei, the Coulomb interactions between one electron and the total density defined by all electrons and the exchange and correlation contribution. The last term includes all the quantum mechanical effects that are not included in the others. The functional form is not known.

To solve these equations, the problem is treated in an iterative way. A trial density is defined and equations are solved with this trial electron density corresponding to a set of electron occupancies to find wave-functions. Electron density corresponding to these wave-functions is then calculated and compared to the trial one to some defined numerical criteria. If they are considered to be different, trial electron density is changed until convergence is reached.

Exchange-correlation functional can just be derived analytically only for a uniform electron gas, where electron density is constant at all points in space. If this is used in a way that exchange-correlation potential at each position is set as the exchange-correlation potential from the uniform electron gas at the electron density observed at each position, only local density is used to define the approximate exchange-correlation functional. Functionals that use this are included in the local density approximation (LDA). Another group of functionals use a generalized gradient approximation (GGA), which uses information about the local electron density but also the local gradient in the electron density. The GGAs are an attempt to improve LDAs.^[22] There is a GGA free of empirical parameters, known as the Perdew-Burke-Ernzerhof-GGA (PBE-GGA) functional that has shown good performance in giving total-energy-dependent properties in good agreement with experiments.^[23]

Concerning the basis set, a plane-wave-basis formalism is the most efficient for periodic structures because of its compactness and its saving in memory. Plane waves are characterized by their energy, so that energy cut-off is the criteria used to define the extension of the basis set, thus the accuracy of the calculation. However, as wave functions of real materials are smooth in the bonding region and oscillating close to the nucleus, a lot of plane waves are needed to describe with suitable accuracy the bonding regions while taking into account the large variations in the atom center. But at the same time core electrons are not especially important in defining chemical bonding.

Therefore, an important approach to reduce computational cost is to use pseudopotentials that replace the electron density from a chosen set of core electrons with a smoothed density chosen. In some core radius, the all-electron wave function is replaced by a soft pseudo-wave function, with the crucial restriction that outside the core radius the pseudopotential and all-electron function are identical. As valence wave functions tend to have rapid oscillations near ion cores because they have to be orthogonal to core states, it is convenient to get smoother pseudo-wave

functions and increase computational efficiency.^[22] One of the state of the art (an in general accepted by the community) method to do it is to use the projector-augmented wave method. This method is based on a linear transformation between smooth pseudo-wave-functions and the true all-electron Kohn-Sham wave functions, so that PAW method is an all-electron method within the frozen core approximation.^[24]

When modelling solid materials, periodic boundary conditions are usually used as a simple way to impose boundary conditions in condensed matter. In other words, infinite Bravais lattice is considered.

It is a convenient method because it is compatible with the use of plane waves as basis sets, which is a powerful and efficient tool when modelling solid systems. It consists in performing the calculation on a portion of the system of interest that is contained in a supercell and repeat it periodically in space. The shape of this cell determines the type of the lattice for the system and is explicitly expressed through vectors and atom positions.

If Schrödinger equation is solved for periodic systems, the solution must satisfy Bloch's theorem. If we solve the Schrödinger equation for periodic systems, the solution must satisfy Bloch's theorem. This theorem states that the solution can be expressed as a sum of terms with the form as shown in **Equation 3**.

$$\Phi_k(r) = \exp(ik \cdot r)u_k(r)$$
 Equation 3

The first term comprises the plane waves and the second term is the periodic part.

Mathematical issues arisen by Bloch functions are more conveniently solved in terms of *k* space, which corresponds to the Fourier transform of real space, and it is commonly known as reciprocal space. The reason for that is that it becomes an integral of a continuous function, and this is a useful mathematical property because numerical methods are easier to develop. A primitive cell can be defined in reciprocal space. It is known as the *Brillouin zone*.

To use this method, the number of k points that are used in each direction in reciprocal space needs to be chosen. This number of k points tends to be a precision label for the calculations. Higher k point sampling leads to more accurate results, until some degree of k-point sampling where precision is not increased considerably, in where calculated properties' values are invariable to further increases in the k-mesh. For calculations with supercells that have the same length along each lattice vector, it is natural to use the same number of k points in each direction. But if the length of the lattice vectors of the supercell is different, different number of k points for each direction should be used. Taking into account the relation between real and reciprocal space, the greater the length of the real vector, the smaller the length of the reciprocal one, and so less k-points are needed. This is what happens when modelling surfaces. As periodic boundary conditions are applied, the slab is repeated in z direction, but this is physically incorrect because a 2D system is being modelled. To tackle this question, empty space is left above the atoms in the top portion of the supercell in the z direction, and it is called vacuum. It is important that there is enough vacuum space so that the electron density of the materials tends to zero in the vacuum to remove the effect of the z-neighboring slabs because of periodic conditions.

As mentioned before, integrals over the Brillouin zone must be evaluated. In some cases, especially for metals, the function that is integrated changes discontinuously. For this cases, the Brillouin zone can be divided into regions that are occupied and unoccupied by electrons. The surface in *k* space that separates these two regions is called the *Fermi surface*. The function that is integrated changes discontinuously from nonzero to zero at the Fermi level, so that there are numerical solving problems when facing this discontinuous part of the function. Very large numbers of *k* points are needed to get well-converged results.

The convergence to the number of k points can be improved by smoothing the function. This can be made in different ways and the smoothing parameter is known as the smearing temperature.^[25]

METHODS

All the calculations in this work are density functional theory (DFT) calculations performed using the Vienna Ab initio Simulation Package (VASP) code. It is a convenient software for atomic scale materials modelling from first principles.^[26]

The Perdew-Becke-Ernzerhof functional (PBE) was employed with inner electrons represented as projector augmented waves (PAW) and dispersion contributions, through the D3 approach. As standard density functional approximations are unable to correctly describe long-ranged London dispersion interactions there is a need to use correction methods to lead to reliable results that take into account these dispersion forces. The DFT-D3 dispersion correction method has shown good performance.^[27] The valence monoelectronic states were expanded in plane waves with a cut-off kinetic energy of 450 eV, which is higher than the suitable cut-off indicated in the pseudopotentials used for all the atoms of the study to ensure good precision

In all cases the ionic and electronic convergence criteria were 10^{-4} eV and 10^{-5} eV, respectively, in the self-consistent field (SCF) cycle. All calculations were unrestricted to take into consideration spin polarization. Gaussian smearing was used with a smearing temperature of 0.05 eV. This method uses a Gaussian function to assign electron occupancies and helps reduce the number of *k*-points needed to solve the equations.

The calculated molecules were placed in triclinic boxes with a suitable size so as to minimize periodic boundary effects. Materials Studio was used to generate the coordinate matrix of the molecules. For slab calculations, a dipole correction was employed along the *z*-direction, to minimize artificial dipole for periodic boundary conditions.

Geometry optimizations were performed by sampling the Brillouin zone with a $3\times3\times1~k$ point grid for the slab structures, while bulk graphite as a $13\times13\times13$ and bulk phosphorus as a $9\times9\times9$, to have approximately equal density of k points in all structures.

A test was developed to optimize the k point density for the slab structures. Gamma-point (1x1x1), 2x2x1, 3x3x1 and 4x4x1 k-point grid were compared in terms of computational time and total energy. Results are shown in **Figure 2**.





As these systems are quite large, a small number of *k*-points is needed. Thus, after increasing he density from gamma point to 2x2x1, the precision of the total energy reaches a convergence. Therefore, as the computational cost is not significantly larger for 3x3x1 mesh, the choice fell to the latter. As the systems are not planar in most of the cases and symmetry becomes easily broken, it is suitable to use a denser *k* point grid to have a better sampling.

Bulk graphite is calculated as a hexagonal crystal structure and bulk phosphorus as alpha phosphorus (body-centered structure) and internal parameters, shape and volume are allowed to relax. Pristine graphite structure is obtained by cleaving the bulk optimized one, and it is calculated as a (6x6) supercell containing 216 atoms in three layers with the first two allowed to relax.

From the derivation of pristine graphite, pristine carbon nitride is calculated as a (6x6) supercell containing 96 atoms of N and 72 atoms of C in three layers with the first two allowed to relax. Among the different phases that exist, g-h-C3N4, a hydrogen-free layered C-N phase of heptazine units connected is modelled.^[28]

These 3-layer models with the first two allowed to relax is chosen so as to take into account surface relaxation effects, since the different coordination of atoms in the surface or in the bulk can lead to different spacing between layers near the surface than in the bulk.

Only internal parameters from the structures derived from the bulk are allowed to relax, since the whole crystallographic structure does not change, so shape and volume is fixed for all the calculations and the values from bulk graphite are kept.^[16]

Defects on graphite-based structures are obtained by atomic substitution of different carbon positions. Eleven different types defects are generated, comprising different ratios of doping respect vacancy creation, different coordinative environments and oxidation levels.

For $g-C_3N_4$ -based structures, seven different types of defects are studied by atomic substitution in heptazines, comprising substitution of each different atomic position and also bi-doped and tridoped ones.

Defect formation energies are calculated as a way to compare its relative stability. They are considered from pristine graphite and pristine graphitic carbon nitride, respectively, as shown in the reaction schemes below. Defect formation energies are calculated referred to pristine graphitic carbon nitride, bulk graphite, bulk phosphorus, nitrogen oxygen and hydrogen, as shown in **Equation 4**, where v_i refers to stoichiometric coefficient and E_i to the DFT total energy for each *i* structure.

Formation energy =
$$\sum_{i=1}^{n} v_i \cdot E_i$$

C₂₁₆ + n P + m/2 O₂ + t/2 H2 \rightarrow C_{216-s}P_nO_mH_t + s C (graphene defects)

 $C_{72}N_{96} + P \rightarrow C_{71}N_{96}P + C (g-C_3N_4C \text{ cavity defects})$

 $C_{72}N_{96} + n P \rightarrow C_{72}N_{96-n}P_n + n/2N_2 (g-C_3N_4 N \text{ cavity defects})$

From the defects studied for graphite and $g-C_3N_4$, Pd-derived structures are also analyzed. Formation energies of these structures are calculated to compare the ability of the supports to anchor Pd. They are calculated referred to the P-doped systems and to Pd atom.

Analysis of the charges is performed using the Bader approach.

Equation 4

The distribution of electrons in chemical systems requires a practical treatment. Experimental and computational techniques are widely used to obtain density maps in solids. However, as atomic charge is not an observable, it needs to be approached. One of the ways to manage the charge assignation is to use the Bader analysis. It does a geometric partitioning using zero flux surfaces to divide atoms, where the charge density is minimum perpendicular to the surface.^[29]

Bader charges are an easy way to assign density to the atoms to compare among them. This data is used together with their XPS relative shifts. Bader charged are calculated for phosphorus in the defect systems and for Pd when it is in cavity.

XPS relative shifts are calculated to explore the different chemical environments. Chemical shifts observed in high-resolution X-ray photoelectron spectroscopy (XPS) spectra are normally used to determine the chemical state of the elements of interest.^[30] XPS determines the binding energy of the electrons and this allows to rationalize about the chemical environment and the oxidation state of the atom of interest. Higher shifts correspond to a higher degree of oxidation. They are calculated as expressed in **Equation 5**.

XPS relative shift =
$$\Delta XPS = \Delta(E_{final} - E_{initial})$$
 Equation 5

The initial state is represented as the electronically relaxed ground state. The Kohn-Sham energy of each core state is recalculated in every step of the self-consistent cycle. To represent the final state, the excited core electron is removed from the system and the electronic structure is modified according to the electron hole. This way of calculating XPS shifts is referred as the final state approximation. Because binding energy is affected by the final state and chemical environments, XPS core-level shifts are calculated considering these effects. Spin polarization is taken into account to model the charged holed systems.

The computational variables values are kept from the geometry optimization. XPS 3d Pd corelevel shifts are calculated for the Pd in cavity for both sets of systems. Furthermore, P 2p XPS shifts are calculated for P-doped graphite to compare with experimental XPS.

Projected Density of States (PDOS) and *d*-band center respect to the Fermi level are studied to explore the electronic properties and how are they affected by doping and Pd. It is explored to understand Pd bonding in the supports, and potential adsorption ability of the metal single atom in a catalytic process.

For the DOS, 11x11x1 *k*-point sampling grid is used, since a finer grid is needed to explore this property.

d-band center is calculated as expressed in **Equation 6**.

$$\varepsilon_{d} = \frac{\int_{E_{0}}^{E_{F}} DOS \cdot E \cdot dE}{\int_{E_{0}}^{E_{F}} DOS \cdot dE}$$

Equation 6

RESULTS AND DISCUSSION

Optimized bulk graphite exhibits a hexagonal cell with cell parameters a=2.464 Å, b=2.464 Å, c=6.918 Å, α = β =90° and γ =120°. Interlayer spacing is found to be 3.458 Å.

According to the three-layer system of pristine graphene, the interlayer spacing becomes 3.465 Å and 3.446 Å for the top layers and the bottom ones, respectively. Changes in interspacing are associated to surface relaxation. Cleaving a surface in a material leads to a different chemical environment of the atoms at the surface, and often this involves a change in the distance between the first and second atomic layers.^[31]

The graphene defects that have been studied are shown in **Figure 3** and classified according to the coordination environment and the number of dopants and vacancies that are generated.

Doping with phosphorus causes large distortions in graphene. When a P atom is inserted into a C cavity, with its sp³ character, bond angles tend to be around 90-100°, far from the 120° typical of sp² character of pristine graphite, so that configurations are more tetrahedral-like, breaking the planarity of pristine graphene.^[32]

P-C bonds are also longer than C-C bonds in graphite, according to a bigger size of phosphorus and a more sp³-like character. P-C bond length is around 1.7-1.9 Å, while C-C for pristine graphite is 1.42 Å.

The increase in the bond length when doping combined with the differences in the bond angles force phosphorus to get out of the plane, getting embedded between the first and second layer for some structures or above the top layer for the others. The exception for this is P1V2, where the two carbon vacancies allow the phosphorus to keep the planar structure of the pristine graphene.

This phenomenon is different for nitrogen-doped graphene-based materials. In this case, as nitrogen can behave with sp² character and has a more similar size to carbon than phosphorus, N-doped structures keep the planar structure of the pristine graphene.^[33]

The distortion that P provides to the planar structure of pristine graphene generates a great variety of coordinative environments and hole widths with a potential versatility in different electronic properties for each case.



Figure 3. Top view of the phosphorus-doped graphene-based structures. Grey colour corresponds to carbon, yellow to phosphorus, white to hydrogen and red to oxygen. Phosphorus Phospholic and phosphorinic coordination are analogue to nitrogen pyrrolic and pyridinic environments, respectively.

In **Table 1**, defect formation energies, P Bader charges and P 2p XPS relative shifts for graphenebased structures are shown and discussed below.

Defect type	E _F (eV)	Bader charges (e ⁻)	XPS Relative Shift (eV) ^a
P1V1	2.29	-1.68	0.00
P3V4	5.58	-1.11, -1.16, -1.17	-0.88
P3V9H3	4.36	-1.20, -1.23	-0.88,-0.93
P1V2	3.31	-1.85	-0.26
P2V2	4.27	-0.83, -0.95	-0.02, 0.01
P2V4	5.02	-1.22, -1.28	0.40, 0.38
P4V6	4.81	-1.01, -1.06, -1.08, -1.12	-0.40, -0.41
P4V8	4.76	-0.85, -1.13, -1.17	-0.88, -0.85, -0.09, -0.14 ^b
P7V14	8.21	-1.12, -1.14, -1.16	-1.01, -1.06, 2.09, 2.88
P101V1	-1.11	-3.06	0.00
P101V2	1.75	-2.54	0.30

Table 1. Formation energy, Bader charges (in units of electrons) and XPS P 2p relative shift of the phosphorus-doped graphene-based structures.

^a XPS shifts are calculated relative to graphitic defect for all structures except the oxidized ones, for which oxidized graphitic defect is chosen as a reference. In case of having more than one phosphorus, just values that are different are shown (XPS and Bader charges)

^b First two correspond to phosphorinic P and last two to phospholic P.

In general, oxidized phosphorus structures are more stable than the others. This can be due to the fact that phosphorus forms a strong bond with oxygen (24.27 eV/bond).^[34] This is observed in **Table 1**, where the P1O1V1 shows exothermic defect energies, in contrast to the others.

Here it is important to underline that the formation energies were defined with bulk reference states to make their cross-comparison more reliable. In reality, these materials would be likely synthesized from energy-richer precursors that would favor the thermodynamics. Keeping this in mind, it can be observed that the generation of a graphitic defect or a single phosphorinic-phospholic site, especially if they are oxidized are the most prone to happen (P1V1, P1V2, P1O1V1 and P1O1V2).

Bader charges are difficult to analyze because of intrinsic problems. Individual atomic charges are not a quantum mechanical observable and there is much ambiguity in the definition and the approaches to calculate them. Nonetheless, Bader charges are shown as a *level-of-oxidation* descriptor.^[29] It can be seen that oxidized phosphorus exhibit the highest charge, as it is expected.

According to experimentally determined XPS shifts as found in the literature, P-doped graphite is identified by the presence of P in different chemical environments, corresponding to P-C and P-O bonds.^{[35][14]} XPS reveals that C is present in its sp² and sp³ form^[34], and XPS P 2p spectra is deconvoluted into three peaks as shown in the bottom part of **Figure 4**: 130.6 eV, 132.5 eV and 134.2 eV, corresponding higher values to higher oxidation state of phosphorus. However, exact coordination of P is not specified, and other possibilities are sparse in the literature.



Figure 4. P 2p core level XPS spectra of the P-doped carbon monolith. Reprinted with permission from Hasegawa, G. *et al.* High-Level Doping of Nitrogen, Phosphorus, and Sulfur into Activated Carbon Monoliths and Their Electrochemical Capacitances. *Chem. Mater.* **27**, 4703-4712 (2015). Copyright 2019 American Chemical Society.^[36]

Analyzing calculated relative shifts, both P1V1, P1V2 and P2V2 present similar XPS shift, despite representing different coordinative environments. Taking into account its similar and low formation energy (especially for P1V1 and P1V2), this open ups the possibility of having both graphitic and phosphorinic-phospholic chemical environments when doping graphene as the most stable ones. According to oxidized structures, their similar XPS shift together with their low formation energy suggests that oxidized phospholic-phosphorinic and oxidized graphitic defect could be commonly obtained when doping with phosphorus.

For the other defects, highly coordinated systems exhibit lower XPS shift, due to charge transfer from phosphorus. It can also be seen that phosphorinic defects exhibit similar XPS shift (around

-0.88 eV) and different from the others, so that it seems that they can be characterized by XPS. However, these coordination environments have not been reported in the literature. The two P-C peaks that are found in experimental works can be assigned to different coordination degrees, as they exhibit very different shifts when changing the number of coordinative bonds. Presenting these two peaks in synthesized P-doped graphene shows the versatility of environments that are generated when the support is post-functionalized by heteroatom doping.

To study the binding ability of the new coordinative sites, Pd is placed in cavity and relative stability and electronic properties are studied. Top views of the optimized structures are shown in **Figure 5**. Pd tends to be located in top of the defects, except for Pd-P4V8, where it is embedded between the top and second layer. The bond lengths are among 2.15-2.35 Å, similar to typical Pd catalysts ^{[37].} For oxidized structures, it tends to coordinate to oxygen, so that it is not located in top of the defect but bridging oxygen and carbon. In some cases, Pd exhibits a square-planar like coordination, resembling common homogeneous catalysts. However, in some other cases its coordination sphere is more free, exhibiting its potential to behave as an active site with good catalytic performance as binding ability is enhanced.

In **Table 2**, the formation energies, Bader charges, Pd 3d XPS shifts and magnetic moments for the Pd-derived defects are shown.

Most stable systems are constituted by the highest coordinated environments. Despite the formation of the P-doped defect was not favorable for P4V6, P4V8 and P7V14, compared to the others, as Pd can bind to phosphorus and get a square-planar like configuration or even fifth-coordinated, the system is stabilized. For the Bader analysis, it can be stated that Pd is presented as Pd(0) for these systems. XPS show that highly coordinated structures lead to a lower shift due to charge transfer from the support to Pd.



Figure 5. Top view of Pd in cavity for the graphene-based structures. Grey colour corresponds to carbon, yellow to phosphorus, white to hydrogen, red to oxygen and cyan to palladium.

Table 2. Characterization data of Pd P-doped graphene-based systems. Formation energy of the Pd-dervied system, Pd Bader charge (I units of electrons), XPS 3p Pd shift and total magnetic moment.

Pd system	E _F (eV)	Pd Bader charge (e)	XPS 3p Pd shift (eV) ^a	μ (μ _в)
Pd-P1V1	-2.57	0.14	0.00	0.01
Pd-P3V4	-2.56	-0.03	-0.67	0.88
Pd-P3V9H3	-4.14	-0.03	-1.37	0.00
Pd-P1V2	-2.17	-0.06	-0.10	0.00
Pd-P2V2	-1.98	-0.04	-0.30	0.00
Pd-P2V4	-3.25	-0.08	-1.56	0.00
Pd-P4V6	-4.64	0.26	-2.63	0.00
Pd-P4V8	-4.19	0.16	-2.18	0.00
Pd-P7V14	-5.53	0.05	-1.40	0.93
Pd-P1O1V1	-1.43	-0.27	1.33	0.79
Pd-P1O1V2	-2.42	-0.41	0.12	0.45

^a XPS 3p Pd shifts are calculated referred to Pd-P1V1.

Spin up and spin down projected total density of states is shown in **Figure 6** and *d*-band center for the Pd-P-doped graphene-based system is shown in **Figure 7**.

Examining the PDOS, it can be seen that phosphorus-doping leads to a great overlapping in low levels of phosphorus carbon and palladium states. Phosphorus exhibits a better coordinative interaction with palladium than carbon. It can also be observed the effects of the coordinative environment in the density of states. As it can be seen, for the highest coordinated systems, P4V6, P4V8 and P7V14, the highest density of states is located lower than for the others respect the Fermi level. A great overlapping between the Pd and the non-metal states can be detected. This enhances the strong bonding between these atoms and the Pd, leading to a closed coordination sphere. Spin up and down density of states is quite similar, as these systems generally present low magnetization.

d-band center follows the same trend. As it can be seen, for these high coordinated systems the *d*-band center is located the furthest from the Fermi leve. This decreases the number of states available for adsorbate interaction, and thus to a higher adsorption energy for potential substrates, so that catalytic activity is more complicated.

These investigations follow what is expected for high coordinated systems. They constitute closed systems where molecules are difficult to bind.



Figure 6. PDOS for Pd-P-doped carbon-based systems. Grey color is used for carbon, orange for phosphorus and cyan for palladium.



Figure 7. Pd *d*-band centre for Pd-P-doped carbon-based systems.

On the other way round, for instance P1V1, P1V2, P1O1V1 and P1O1V2 present low-coordination spheres. In these systems, overlapping of *d* states with non-metal states is lower, and they present a higher density of states in energy intervals closer to the Fermi level. As *d*-band center is then located also closer to the Fermi level in comparison with the other systems, a much lower adsorption energy is hoped to be presented towards potential substrates. For this reason, they are expected to have better catalytic performance.

P1O1V1 is the most stable P-doped system and at the same time exhibits the best potential catalytic performance, as it has the highest *d*-band center. However, Pd-derived system formation is not the most favorable, due to a low coordination of the palladium atom in the support. On the other hand, P7V14 is the less stable P-doped structure. Besides this, it does not exhibit a good binding ability because of a low *d*-band center. Nevertheless, its Pd-derived system shows better stability than the other systems, but this can be explained in terms of the high coordinated system that is obtained when palladium is placed in cavity.

To sum up, P1O1V1 shows the best catalytic performance and viability of obtaining the material, followed by P1O1V2, P1V1 and P1V2.

For graphitic carbon nitride-derived structures, the defects are shown in **Figure 8** and classified according to atomic substitution and degree of doping.



Figure 8. Top views of the defects in graphitic carbon nitride. Blue is used for nitrogen, grey for carbon and yellow for phosphorus. *d* and *f* correspond to the same structure.

Unlike pristine graphene, graphitic carbon nitride is not planar. Instead of this, it presents buckling that breaks the symmetry. This has been reported in a thermodynamic study that explored relative stability of different phases of graphitic carbon nitride related to experimental conditions.^[28]

When doping with phosphorus, buckling is emphasized. Due to phosphorus larger size and its sp³-character, it tends to generate considerable distortions. C-N bond angles change from 117-124° to around P-N and P-C bond angles of 90-110° for all the structures. C-N bond lengths change from 1.34-1.41 Å to around 1.60-1.80 Å for P-N and around 1.80-1.90 Å for P-C, due to a more tetrahedral-like configuration.

All these structural differences that are generated from doping lead to a preferential occupancy of phosphorus for the interstitial sites in the interlayer region. This corresponds to what has been obtained in previous studies.^[16]

In Table 3, defect formation energies per phosphorus atom added and Bader charges are shown.

Table 3. Defect formation energies and Bader charges of the P atom (in units of electrons) in carbon nitride-based structures.

Defect	E _F (eV/P atom)	Bader charges (e ⁻)
C1	0.42	-2.48
C2	-0.18	-2.38
N1	1.60	-1.22
N2	0.05	-1.17
N3	0.01	-1.44
N2-bidoped	0.22	-1.11, 1.19
N2-tridoped	0.11	-1.14, 1.14, 1.11

From the calculated defect formation energies, it can be concluded that C2 vacancy is the most stable. It can also be observed that C2 defect is more stable than C1, corresponding to what other studies reported.^[15] For N vacancies, it can be seen that the substitution of the three-fold nitrogen inside the heptazine units is the less favourable.

Besides this, a higher degree of phosphorus doping leads to a decrease in the stabilization of the defect. The P atom Bader charges are higher for C vacancy defects. This is due to the fact that as phosphorus has one more electron than carbon, when placing phosphorus in a carbon position it forms the three covalent bonds with four electrons, as carbon does, and the remaining one is delocalized in the structure.^[15] This leads to a decrease on the electronic density for the phosphorus respect N vacancy defects, where the number of valence electrons is not changed when the dopant is placed.

Pd-derived structures are studied and shown in Figure 9.



Figure 9. Top view of the Pd in cavity for the phosphorus-doped graphitic carbon nitride-based structures. Grey is used for carbon, blue for nitrogen, yellow for phosphorus and cyan for palladium.

Pd tends to stay trapped in the cavity, which means a good performance of these materials as supports. It tends to be more coordinated than P-doped graphene-based structures, because it is for some of the structures coordinated to phosphorus and also nitrogen.

In **Table 4**, Pd-systems formation energies, together with Bader charges, Pd 3d XPS shifts and total magnetic moments are shown.

Table 4. Formation energies, Bader charges, Pd 3d XPS shifts and total magnetic moments forPd in cavity systems.

Pd system	E _F (eV)	Pd Bader charge (e)	XPS 3p Pd shift (eV)ª	μ (μ _Β)
Pd-C1	-3.56	-0.56	0.05	1.00
Pd-C2	-3.75	-0.58	0.00	1.00
Pd-N1	-2.78	-0.57	0.67	0.00
Pd-N2	-3.06	-0.29	0.54	-0.02
Pd-N3	-2.32	-0.52	1.51	0.00
Pd-N2-bidoped	-3.45	0.03	0.07	0.00
Pd-N2-tridoped	-3.85	0.01	0.20	0.00

^a XPS shifts relative to Pd-C2.

Again, adsorption of Pd is more favourable in the highest coordinated systems. Their formation energy is lowered by Pd bonding to three atoms of phosphorus or nitrogen or even four.

Dynamics has to be taken into consideration, so that coordination of Pd could depend on other adsorbed molecules and if they are participating in a reaction, for instance. However, its generally low coordination opens up the possibility of exhibiting good catalytic performance, as their free binding environment would enhance the chance of adsorbing molecules.

Bader charges suggest that Pd is in its Pd(0) form. XPS shifts follow the expected trend. They are lower for more reduced systems, according to highly coordinated systems.

To understand electronic properties in the new systems, total density of states is studied. PDOS is shown in **Figure 10** and *d*-band centre in **Figure 11**. Grey is used for carbon, light blue for nitrogen, orange for phosphorus and cyan for palladium. Spin up and down are represented up and down.



Figure 10. PDOS for Pd-P-doped g-C₃N₄-derived systems.



Figure 11. Pd *d*-band centre for Pd-carbon nitride-based systems.

As these systems doesn't exhibit high magnetic moments, spin up and spin down density of states is similar.

The most important trend can be seen in the comparison of N2, N2-bidoped and N2-tridoped system. As it can be seen in **Figure 10**, free *d* Pd states are located in an upper energy interval as doping degree increases. This leads to a higher degree of available states for binding substrates as doping degree increases, as they are closer to the Fermi level and more empty antibonding states will be presented when interacting with an atomic or molecular adsorbate.

Despite this, this trend is not followed according to the *d*-band centre plot. This is due to the system and the intrinsic problems in calculating the *d*-band centre due to the formulation of the *d*-band model. The *d*-band model was constructed considering metal surfaces with metallic bonds between atoms. Those give rise to a narrow *d*-band close to the Fermi level. However, when an isolated Pd atom is present, the Pd states resemble a molecular complex, with a significant number of states deep below the Fermi level. This makes the *d*-band center sensitive to the integration borders.^[26] For these reasons, here the results do not correspond to what can be extracted from the PDOS.

These bi-doped and tri-doped systems also exhibit a larger overlap between the *d* states and the non-metal ones as doping degree increases, so that anchoring on the support is stronger, and for this reason formation energy is lower for bi-doped and tri-doped systems.

Among C vacancies, similar behaviour is presented. There is a significant overlap between nonmetal and metal states, which leads to a low formation energy compared to N vacancy monodoped systems. Both N vacancy and C vacancy systems exhibit a lower metal density of states near the Fermi level, which indicates that adsorbate binding would be more difficult for these systems.

The system that provide the best hopes for catalytic performance is tridoped-N2, followed by bidoped-N2. Despite this, they do not exhibit the lowest phosphorus defect formation energy. As formation energies are calculated referred to bulk, they are useful in a comparative way but absolute values could be different, as it was explained before in this work. As in experimental conditions thermodynamics is hoped to be favoured, although higher degree of doping leads to less stabilization per defect, poly-doped systems could be also obtained. The corresponding Pd-derived structures present a low formation energy. These results lead to a significant viability for obtaining the materials.

The other structures can be considered to exhibit similar catalytic potential, which is significantly worse than for the bi- and tri- doped for a lower substrate binding ability. Performance comparison among them could then be done in terms of stability and availability of their obtaining. But they are not as interesting as the ones exhibiting more favourable adsorption energies.

The trend that is presented here defers from graphene-based systems. In carbon nitride-based structures, a better binding ability is presented for high coordinated systems, while it is the contrary for the other set of structures, due to the different electronic changes induced by phosphorus doping in these structures. Despite this, morphology of both sets of species has to be taken into account. Both are metal single atoms anchored on a support, so despite having different coordination environments, as they are trapped in 2D systems, they all exhibit a free environment above the surface.

CONCLUSIONS

In this study, a rational way of exploring new palladium single atom heterogeneous catalysts is presented. Potential catalytic performance is predicted using activity descriptors and viability of these materials is also assessed in terms of comparing their stability and measurable (site geometry, core level shifts). These two features are taken into consideration to identify the most promising supported Pd(0) catalysts among two different sets of phosphorus-doped carbon-based materials. According to the graphene-based materials, P1O1V1 presents the most outstanding properties, and tridoped-N2 is the best $g-C_3N_4$ -derived candidate.

In this work, phosphorus doping is presented as an effective way to modify active sites and generate different chemical environments. A pool of potential coordination environments in graphene is explored, as well as the modification of already-existing coordination sites in carbon nitride to improve Pd single atom catalytic properties. This study demonstrates the ability of tailoring the electronic properties of graphene and graphitic carbon nitride via phosphorus doping.

A theoretical rationalization is employed to explore catalytic potential. Favorable trends in the electronic structure have been observed. In addition, these systems are found to be stable and predicted to have good affinity for binding substrates. Conventional principles are applied to provide a rational way to investigate materials' properties. Electronic structure constitutes a central tool in this work to compare structures' properties. However, as SAHCs exhibit homogeneous and heterogeneous behavior, extensive research should be done to adapt standard theories to the description of these materials. Catalytic performance should be in the future discussed as a result of computing reaction mechanisms.

In conclusion, this study switches the conventional way of thinking about palladium catalysts. Coordinative environments of the presented systems are different from state-of the-art squareplanar Pd(0) catalysts, as single metal atoms are anchored on a surface. Pd(0) SAHCs supported on phosphorus-doped carbon-based materials can bridge homogeneous and heterogeneous catalysis to improve the performance respect Pd soluble complexes or nanoparticles. First achievements towards the heterogenization of single atom Pd catalysts on P-doped carbons are presented.

CONCLUSIONS

En aquest treball es presenta un mètode racional per tal d'investigar nous catalitzadors "single atom" de pal·ladi, per tal de predir l'activitat catalítica presentada utilitzant descriptors i la viabilitat dels materials comparant la seva estabilitat i alters propietats (geometria, desplaçament XPS). Aquestes investigacions es tenen en compte per tal d'identificar els catalitzadors de Pd(0) de millors característiques de cadascun dels dos grups de materials de carboni dopats amb fósfor. Pel que fa als materials basats en grafè, P1O1V1 és el més prometedor, mentre que pels derivats de g-C₃N₄ ho és el tridopat-N2.

El dopatge amb fósfor es presenta com una manera efectiva per a modificar els llocs actius I generar diversos entorns químics. Una diversitat de llocs de coordinació s'han creat en el grafè i s'han modificat els del nitrur de carboni per tal de millorar les propietats enllaçants. A més, aquests estudi demostra la capacitat del fósfor per tal de modificar les propietats electròniques del grafè i del nitrur de carboni.

L'activitat catalítica és predita de manera teòrica i aquests sistemes han demostrat bones tendències en l'estructura electrònica i l'estabilitat i presenten bones propietats enllaçants per a adsorbir substrats. En futures investigacions es podrien estudiar els mecanismes de reacció d'algun camp d'aplicació concret per a estudiar amb més certesa l'activitat catalítica.

En aquest estudi s'apliquen principis convencionals per a investigar les propietats dels materials. L'estructura electrònica constitueix una eina principal per a comparar les propietats dels diferents suports. Però, com que els SAHCs presenten un comportament a mig camí entre la catàlisi homogènia i l'heterogènia, cal realitzar una investigació profunda per tal d'adaptar les teories estàndard a aquest grup de materials amb propietats tan específiques per tal de millorar la precisió i adaptabilitat d'aquests principis.

Finalment, cal dir que aquest estudi propicia un canvi en la concepció dels catalitzadors de pal·ladi. Els entorns químics que presenten els sistemes d'aquest estudi són ben diferents dels típicament presentats pels catalitzadors pla-quadrats de Pd(0), ja que aquests es troben enllaçats a una superfície. Els SAHCs de Pd(0) suportats sobre materials de carboni dopats amb fósfor poden unir els avantatges de la catàlisi homogènia i heterogènia per a millorar l'activitat respect eels complexos solubles o les nanopartícules de pal·ladi. S'han dut a terme els primers passos per a l'heterogenització dels catalitzadors de pal·ladi sobre carboni dopat amb fósfor.

REFERENCES

- 1. Kovalenko, M. V. *et al.* Tunability and Scalability of Single-Atom Catalysts Based on Carbon Nitride. *ACS Sustain. Chem. Eng.* (2019).
- 2. Centi, G. & Perathoner, S. Selective Oxidation—Industrial. *Encycl. Catal.* **77**, 287-297 (2003).
- 3. Li, H., Zhang, H. X., Yan, X. L., Xu, B. S. & Guo, J. J. Carbon-supported metal single atom catalysts. *Xinxing Tan Cailiao/New Carbon Mater.* **33**, 1-11 (2018).
- 4. Chen, F., Jiang, X., Zhang, L., Lang, R. & Qiao, B. Single-atom catalysis: Bridging the homo- and heterogeneous catalysis. *Chinese J. Catal.* **39**, 893-898 (2018).
- 5. Liu, J., Bunes, B. R., Zang, L. & Wang, C. Supported single-atom catalysts: synthesis, characterization, properties, and applications. *Environ. Chem. Lett.* **16**, 477-505 (2018).
- Giannakakis, G., Flytzani-Stephanopoulos, M. & Sykes, E. C. H. Single-Atom Alloys as a Reductionist Approach to the Rational Design of Heterogeneous Catalysts. *Acc. Chem. Res.* 52, 237-247 (2019).
- 7. Tyo, Eric C.; Vadja, Stefan. Catalysis by clusters with precise numbers of atoms. *Nat. Nanotechnol.* **10**, 577-588 (2015).
- 8. Parkinson, G. S. Unravelling single atom catalysis: The surface science approach. *Cuihua Xuebao/Chinese J. Catal.* **38**, 1454-1459 (2017).
- Wang, A., Li, J. & Zhang, T. Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* 2, 65-81 (2018).
- 10. Deng, D. *et al.* Catalysis with Two-Dimensional Materials Confining Single Atoms: Concept, Design, and Applications. *Chem. Rev.* **119**, 1806-1854 (2018).
- Vorobyeva, E. *et al.* Tailoring the framework composition of carbon nitride to improve the catalytic efficiency of the stabilised palladium atoms. *J. Mater. Chem. A* 5, 16393-16403 (2017).
- 12. Haag, D. & Kung, H. H. Metal free graphene based catalysts: A review. *Top. Catal.* **57**, 762-773 (2014).
- Yu, J., Cheng, B., Zhu, B., Tong, T. & Jiang, C. Mechanistic insight into the enhanced photocatalytic activity of single-atom Pt, Pd or Au-embedded g-C 3 N 4. *Appl. Surf. Sci.* 433, 1175-1183 (2017).
- 14. Routh, P. *et al.* Boron-nitrogen-phosphorous doped graphene nanoplatelets for enhanced electrocatalytic activity. *Eur. Polym. J.* **99,** 511-517 (2018).

- 15. Ran, J., Ma, T. Y., Gao, G., Du, X. W. & Qiao, S. Z. Porous P-doped graphitic carbon nitride nanosheets for synergistically enhanced visible-light photocatalytic H2production. *Energy Environ. Sci.* **8**, 3708-3717 (2015).
- 16. Zhou, Y. *et al.* Brand new P-doped $g-C_3N_4$: Enhanced photocatalytic activity for H₂ evolution and Rhodamine B degradation under visible light. *J. Mater. Chem. A* **3**, 3862-3867 (2015).
- Martin, R. & Buchwald, S. L. Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions Employing Dialkylbiaryl Phosphine Ligands. *Acc. Chem. Res.* 41, 1461-1473 (2008).
- Biffis, A., Centomo, P., Del Zotto, A. & Zecca, M. Pd Metal Catalysts for Cross-Couplings and Related Reactions in the 21st Century: A Critical Review. *Chem. Rev.* **118**, 2249-2295 (2018).
- 19. Midgley, P. A. *et al.* A heterogeneous single-atom palladium catalyst surpassing homogeneous systems for Suzuki coupling. *Nat. Nanotechnol.* **13**, 702-707 (2018).
- Hammer, B.; Nørskov, J. K. Theoretical Surface Science and Catalysis Calculations and Concepts. *Adv. Catal.* 45, 71-129 (2000).
- 21. Roald, H. How Chemistry and Physics Meet in the Solid State. *Angew. Chemie Int. Ed. English* **26**, 846-878 (1987).
- 22. sholl, D. S.; Steckel, J. A. What is density functional theory? In Density Functional Theory: A Practical Introduction. New Jersey, 2009; pp.7-15.
- Madsen, G. K. H. Functional form of the generalized gradient approximation for exchange: The PBEα functional. *Phys. Rev. B* **75**, 195108 (2007).
- Enkovaara, J. *et al.* Electronic structure calculations with GPAW: A real-space implementation of the projector augmented-wave method. *J. Phys. Condens. Matter* 22, (2010).
- Sholl, D. S.; Steckel, J. A. Nuts and Bolts of DFT Calculations. In Density Functional Theory: A Practical Introduction. New Jersey, 2009; pp 49-78.
- Fako, E., Łodziana, Z. & López, N. Comparative single atom heterogeneous catalysts (SAHCs) on different platforms: A theoretical approach. *Catal. Sci. Technol.* 7, 4285-4293 (2017).
- 27. Schröder, H., Hühnert, J. & Schwabe, T. Evaluation of DFT-D3 dispersion corrections for various structural benchmark sets. *J. Chem. Phys.* **146**, (2017).
- Botari, T., Huhn, W. P., Lau, V. W. H., Lotsch, B. V. & Blum, V. Thermodynamic Equilibria in Carbon Nitride Photocatalyst Materials and Conditions for the Existence of Graphitic Carbon Nitride g-C₃N₄. *Chem. Mater.* **29**, 4445-4453 (2017).

- 29. Walsh, A., Sokol, A. A., Buckeridge, J., Scanlon, D. O. & Catlow, C. R. A. Oxidation states and ionicity. *Nat. Mater.* **17**, 958-964 (2018).
- 30. Tardio, S. & Cumpson, P. J. Practical estimation of XPS binding energies using widely available quantum chemistry software. *Surf. Interface Anal.* **50**, 5-12 (2018).
- Olmsted, J. A. Synthesis of Aspirin: A General Chemistry Experiment. J. Chem. Educ. 75, 1261 (1998).
- 32. Cruz-Silva, E. et al. Electronic Transport and Mechanical. ACS Nano 3, 1913-1921 (2009).
- 33. Kaiser, S. K. *et al.* Controlling the speciation and reactivity of carbon-supported gold nanostructures for catalysed acetylene hydrochlorination. *Chem. Sci.* **10**, 359-369 (2019).
- 34. Dutton, S. E. *et al.* Synthesis and extensive characterisation of phosphorus doped graphite. *RSC Adv.* **6**, 62140-62145 (2016).
- 35. Ren, J. *et al.* A reduced graphene oxide/nitrogen, phosphorus doped porous carbon hybrid framework as sulfur host for high performance lithium-sulfur batteries. *Carbon N. Y.* **140**, 30-40 (2018).
- Hasegawa, G. *et al.* High-Level Doping of Nitrogen, Phosphorus, and Sulfur into Activated Carbon Monoliths and Their Electrochemical Capacitances. *Chem. Mater.* 27, 4703-4712 (2015).
- Bei, X., Turner, H. W., Weinberg, W. H., Guram, A. S. & Petersen, J. L. Palladium/P,Oligand-catalyzed suzuki cross-coupling reactions of arylboronic acids and aryl chlorides. Isolation and structural characterization of (P,O)-Pd(dba) complex. *J. Org. Chem.* 64, 6797-6803 (1999).

ACKNOWLEDGMENTS

I gratefully acknowledge Prof. Núria López for giving me the opportunity to start my research career in such an excellent group. I also want to thank my colleagues, who after this stay they have become friends. As well, I am very grateful to Dr. Mar Reguero, who has advised me through the work.

Lastly, I would like to express my gratitude to Edvin Fako, my advisor and supervisor, for his patience, motivation and immense knowledge.