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
Co-director: Edvin Fako
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Contents

• Introduction
• Objectives
• Methods
• Results and discussion
• Conclusions
Introduction

Single-atom catalysis:
Atomic efficiency
Optimal catalytic performance
Bridge homo- and heterogeneous catalysis


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2D supports
Phosphorus doping to tune electronic properties to improve catalysis

Introduction

Single-atom catalysis:
Atomic efficiency
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State-of-the-art C-C coupling catalysts: homogeneous Pd(II) catalysts.

2D supports
Phosphorus doping to tune electronic properties to improve catalysis


Objectives

• Compare different phosphorus-doped carbon-based materials for being used as single atom catalyst supports.

• Assess potential catalytic activity of the corresponding Pd-derived systems.
Methods

Computed DFT parameters
- Formation energy
- XPS shifts
- Bader charges
- Density of states

Computational details
- VASP code
- Plane-wave basis set with an energy cut-off of 450 eV.
- 3x3x1 k-points

11 P-doped systems and corresponding Pd-derived structures
7 P-doped systems and corresponding Pd-derived structures

## Results and discussion

P-doped graphite-based systems and their formation energy (eV)

<table>
<thead>
<tr>
<th>Oxidized</th>
<th>Phosphoric - phosphorinic</th>
<th>Phosphorinic</th>
<th>Graphitic</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1O1V1</td>
<td>4.81</td>
<td>3.31</td>
<td>5.58</td>
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<tr>
<td>P1O1V2</td>
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<td>P7V14</td>
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<td>P4V6</td>
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<tr>
<td>P4V8</td>
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<tr>
<td>P2V4</td>
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<tr>
<td>P1V2</td>
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<td>P2V2</td>
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<tr>
<td>P3V4</td>
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<td></td>
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<tr>
<td>P1V1</td>
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</tr>
</tbody>
</table>

Structures exhibit large distortions.

Oxidized structures are more stable.

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Results and discussion

P-doped graphite-based systems and XPS shifts

XPS shifts: chemically different P atoms exhibiting similar shifts.

## Results and discussion

Pd-P-doped graphite-based systems and their formation energy (eV)

<table>
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<tr>
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<th>Phosphorinic</th>
<th>Graphitic</th>
</tr>
</thead>
<tbody>
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<td>Pd-P1O1V2</td>
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<td>Pd-P3V4</td>
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<td>Pd-P3H3V9</td>
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<tr>
<td>Pd-P1V1</td>
<td>-2.57</td>
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</tbody>
</table>

**Structure:** Pd exhibits a free coordination environment.

**Relative stability:** most coordinated systems are the most stable.

**Bader analysis:** Pd (0).
Results and discussion

Pd-P-doped graphite-based systems: electronic structure

$\sigma$ coupling

Highly coordinated systems

Pd-P1O1V1
Pd-P1V1
Pd-P1V2

$\sigma$ orbital

Metal $d$-Band

$(d-\sigma)^*$

$\epsilon_r$

Pd-pristine-graphite

Pd-P4V6

Pd-P1O1V2

$E-E_F$ / eV

Results and discussion

P-doped carbon-nitride-based systems and their formation energy (eV)

- C vacant
  - C1: 0.42
  - C2: 0.18

- N vacant
  - N1: 1.60
  - N2: 0.05
  - N3: 0.01

- Polisubstituted
  - N2-monodoped: 0.05
  - N2-bidoped: 0.22
  - N2-tridoped: 0.11

Phosphorus is embedded in the interlayer.

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Results and discussion

Pd-doped carbon-nitride-based systems and their formation energy (eV)

Structure: Pd trapped in the cavity and free coordination environment.

Bader charges: Pd(0).
Results and discussion

Pd-doped carbon-nitride-based systems: electronic structure

Higher degree of doping leads to a lower adsorption energy.
Results and discussion

Most promising catalytic systems
Conclusions

• Phosphorus doping is an effective way to modify active sites and generate different chemical environments.
• Presented systems are found to be stable and predicted to have good binding properties.
• Theoretical rationalization is employed to explore catalytic potential.
• First achievements towards heterogenization of C-C coupling reactions are done.
Acknowledgments