Adsorption of thiophene on metal doped Phosphorene; a density functional theory study

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Abstract
In this study, the adsorption of thiophene on the nano-sheet of pristine and the metal doped phosphorene (M=Sc, Ti, Cr, Mn, Fe, Co and Ni) was investigated using density functional theory (DFT) method. The results revealed that the metal doped phosphorene could be used as an efficient surface for thiophene removal. The PDOS analyses have been employed to shed light on the role of the metal dopants (in complex) and thiophene molecule during adsorption. The Sc- and Ti-doped surfaces were found to be more suitable for the adsorption of thiophene in comparison to other metal doped surfaces.

Introduction
Nowadays, more than 80% of the required Energy is obtained from the fossil fuels and the combustion of these fuels is the most important factor in increasing the air pollution. As a result, the reduction of fuel impurities is so important [1]. The presentation of sulfur compounds in the fuel is one of the most important sources of contamination. In recent years, the environmental degradation effects of these substances has led to stricter standards in order to reduce the concentration of them in the fuel mixture. At present, the total sulfur content of gasoline and diesel fuel in Europe should be less than 15 ppm, which is the same as it is in the United States [2].

The study of effective catalysts in the adsorption of sulfur compounds using both the experimental and computational methods has been the subject of numerous articles [3, 4]. The most commonly used desulphurization process in the industry is Hydrodesulfurization (HDS), which is a catalytic process at high temperature and pressure. In the HDS process, most of the remaining sulfur compounds are thiophene and its derivatives, which are important for adsorption and removal processes. However, the removal of aromatic sulfur compounds such as thiophene, benzothiophene and dibenzothiophene costs so much this way and reduces the octane number of gasoline [5]. Therefore, for deep sulfur depletion of gasoline and diesel, other methods are suggested, including: oxidative desulfurization (ODS) [6], extractive desulfurization [7], biodesulfurization [8] and adsorptive desulfurization. In order to the remove the thiophene and its derivatives by the absorption process, different adsorbents have been investigated, such as different alumina surfaces [9], intermediate metal surfaces [10] and metal organic frameworks (MOFs) [11].

Thiophene is one of the volatile organic compounds (VOCs) which due to its high vapor pressure can be easily released. Many studies have been conducted on the biological effects of thiophene indicate that it is a carcinogen and mutagen substance [12]. Therefore, it is necessary to consider methods for the adsorption and the elimination of thiophene [13, 14].

After discovering the two-dimensional materials, their unique chemical and physical properties along with their application were found to be of interest to the researchers [15]. The adsorption of sulfur compounds by graphene was the subject of many articles [16–19]. The adsorption and removal of thiophene and its derivatives by graphene has also been studied [20, 21].

Although black phosphorus is well known for about a century, it has drawn the attention of researchers again in the recent years. The ability of phosphorus to create a two-dimensional structure (2D) which is called...
phosphorene is one of the most important properties of this compound. The phosphorene structure is curved and due to its large surface-to-volume ratio, this material has been developed as a suitable substrate for adsorption [22]. Phosphorene has been studied as a substance for the storage of H2 gas [23, 24]. Adsorption of methanol [25] and dioxane derivatives [26] have also been investigated on the phosphorene sheet. The adsorption of combustion gases on the phosphorene surface has also been studied [27–30].

In this paper, the adsorption of thiophene on pristine phosphorene and intermediate metal doped phosphorene nano-sheets was studied by the DFT method. Due to its unique properties, phosphorene has been selected as the adsorbent. Structural and energy properties of doped phosphorene were studied previously [31, 32]. Previous results indicate that the transition metals dopants can help to improve the adsorption ability of phosphorene [24, 28] so the transition metals M={Sc, Ti, Cr, Mn, Fe, Co and Ni} were replaced in phosphorene nano-sheets in order to get a better adsorbent and the best position of the thiophene ring was proposed on these surfaces.

Considering that the study of phosphorene is of the interest to the researchers, the results of this study can help clarify the behavior of this substance in the adsorption of other molecules.

Computational methods

In this study, the Quantum ESPRESSO package was used for the calculations of density functional theory (DFT). All calculations were performed by using the generalized gradient approximation (GGA) and the Perdewe Burkee Ernzerhof (PBE) functional for the exchange-correlation energy of electronic interactions. For all of these calculations, spin polarized calculations were performed. To consider the long-range interaction, the Van der Waals (vdW) correction proposed by Grimme-D2 was applied.

The first Brillouin zone was sampled employing a Monkhorst-pack grid corresponding to \(4 \times 4 \times 1\) k-point grid for all calculations of geometrical optimizations and electronic properties. Population analysis by the Mulliken method was performed in order to estimate the charge transfer. Primary model for the pristine phosphorene sheet was a \(4 \times 4 \times 1\) periodic super cell, including 64 phosphorus atoms. The 20Å vacuum thickness along the perpendicular direction was added to avoid neighboring interactions.

In order to find the doping energy for Metal doped phosphorene, the cohesive energy (\(E_{coh}\)) of the metals to phosphorene is calculated by using the equation below:

\[
E_{coh} = E_{complex} - E_{phosphorene} + E_{phosphorus} - E_{dopant}
\]

Where \(E_{complex}, E_{phosphorene}, E_{phosphorus}\) and \(E_{dopant}\) are the total energies of the metal doped phosphorene, pristine phosphorene, isolated phosphorus atom and isolated metal atom respectively. This equation shows the energy difference between the pristine phosphorene and metal doped phosphorene sheets [33].

The adsorption energy (\(E_{ads}\)) of the thiophene molecule on phosphorene or metal doped phosphorene is calculated by:

\[
E_{ads} = E_{sheet + thiophene} - E_{thiophene} - E_{sheet}
\]

Where \(E_{thiophene}, E_{sheet}\) and \(E_{sheet + thiophene}\) are the total energies of the isolated thiophene molecule, isolated phosphorene/metal doped phosphorene sheet and the phosphorene/metal doped phosphorene-thiophene complex, respectively.

Results and discussion

Thiophene adsorption on pristine phosphorene

In the optimized \(4 \times 4 \times 1\) periodic super cell of phosphorene (64 phosphorous atoms), the length of the p-p bonds in the direction of zigzag (\((r_{P-P})_{zigzag}\)) and armchair (\((r_{P-P})_{armchair}\)) are 2.262 Å and 2.279 Å respectively and the bond angles are 99.8° and 101.50°, respectively, which are consistent with the previous results [24–26]. Figure 1 shows the optimized geometry of pristine phosphorene.

In order to obtain the best adsorption configuration, the thiophene molecule was brought close to the phosphorene plate in various positions. The four configurations of figure 2 are the result of structural optimization calculations.

In the structure A, the thiophene molecule is parallel to the phosphorene surface and perpendicular to the zigzag direction, while in the B position, the thiophene molecule is rotated 90 degrees and is parallel to the zigzag direction. In the structures C and D, the thiophene molecule is vertical to the surface of phosphorene, C: downward and D: upward.
The adsorption energy ($E_{\text{ads}}$), the minimum distance of the sulfur atom of thiophene from the phosphorene plate ($d_{(S-P)}$), the S–C bond length ($r_{(S-C)}$) in the thiophene molecule and charge transfer to phosphorene sheet in four situations including: A, B, C and D, obtained after the optimization, are represented in Table 1.

The arrangement of the adsorption energies is: $E_{\text{ads},A} > E_{\text{ads},B} > E_{\text{ads},C} > E_{\text{ads},D}$ whose values are $-0.50, -0.47, -0.31, -0.24$ eV respectively. The adsorption energies of the structures A and B are larger than that of the other two structures, indicating that the most stable adsorption structure is when the thiophene molecule is parallel to the phosphorene plate and is not required to be vertical or parallel with the armchair direction. The amount of adsorption energies are in line with the physical adsorption.

The results appeared in Table 1 show that the bond length of the S–C in the adsorbed thiophene molecule has increased from 1.730 Å to 1.732 Å in comparison to the free thiophene molecule. Investigating the Mulliken population analysis shows that the charge transfer occurs from the thiophene molecule to the phosphorene plate. As shown in Table 1, the adsorption energy increases with increasing the amount of charge transfer.
Figure 3 shows the PDOS diagrams of pristine phosphorene and the PDOS diagrams of phosphorene sheet after the adsorption of thiophene (phosphorene in complex) in structure A, which has the highest adsorption energy. Figure 3(b) represents the PDOS of thiophene molecule. As shown in figure 3, the p orbitals of phosphorene have slightly grown after thiophene adsorption. Electron charge transfer from thiophene to the phosphorene plate and overlapping of the thiophene p orbitals with p orbitals of phosphorene (in the range of 0 to −6 eV) can be the reason of this growth. The results show that there is a little interaction between thiophene and pristine phosphorene plate. In order to reform the structure and increase the interaction with thiophene, the intermediate metal atoms (M = Sc, Ti, Cr, Mn, Fe, Co and Ni) were doped into the phosphorene structure and the interaction of thiophene with these structures were investigated.

**Metal doped phosphorene**

Previous studies have shown that phosphorene doped surface can increase the adsorption efficiency of some compounds [24–30]. To the best of our knowledge, the metal doped phosphorene surface has not been investigated for the purpose of thiophene adsorption; therefore, in this study, the surface of phosphorene doped with a single atom of intermediate metal M = (Sc, Ti, Cr, Mn, Fe, Co and Ni) was used for the adsorption of the thiophene molecule.

The surface of metal doped phosphorene was made by replacing a phosphorus atom with an intermediate metal atom. Figure 4 shows the initial structure of metal replacement.

Figure 4 shows the PDOS for thiophene-phosphorene system: (a) phosphorene sheet, (b) thiophene molecule.

Figure 4. Initial structure of metal replacement.

Figure 3(a) shows the PDOS diagrams of pristine phosphorene and the PDOS diagrams of phosphorene sheet after the adsorption of thiophene (phosphorene in complex) in structure A, which has the highest adsorption energy. Figure 3(b) represents the PDOS of thiophene molecule. As shown in figure 3, the p orbitals of phosphorene have slightly grown after thiophene adsorption. Electron charge transfer from thiophene to the phosphorene plate and overlapping of the thiophene p orbitals with p orbitals of phosphorene (in the range of 0 to −6 eV) can be the reason of this growth. The results show that there is a little interaction between thiophene and pristine phosphorene plate. In order to reform the structure and increase the interaction with thiophene, the intermediate metal atoms (M = Sc, Ti, Cr, Mn, Fe, Co and Ni) were doped into the phosphorene structure and the interaction of thiophene with these structures were investigated.

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The optimization of this sheet was done using the same conditions. Figure 5 shows the optimized structure of phosphorene at the metal substitution zone. As shown in figure 5, the metal is protruding from the plate and a curvature has been created in the zigzag row. The bond length of metal–phosphorus (r(M–P)_{zigzag} and r(M–P)_{armchair}) has been provided in table 2. The bond length of the M-P in both zigzag and armchair...
directions was increased in comparison to the phosphorene sheet but decreased from Sc to Ni replacement, which is in agreement with the Covalent radius of these intermediate metals:

\[
\text{Sc} > \text{Ti} > \text{Cr} > \text{Mn} > \text{Fe} > \text{Co} > \text{Ni}.
\]

The cohesive energy of the metal to the phosphorene sheet \(E_{\text{coh}}\) is calculated by using the equation (1), and the results are reported in table 2. The order of the cohesive energies appears in this way: \(E_{\text{coh}, \text{Sc}} \approx E_{\text{coh}, \text{Ti}} > E_{\text{coh}, \text{Co}} > E_{\text{coh}, \text{Ni}} > E_{\text{coh}, \text{Fe}} > E_{\text{coh}, \text{Cr}} > E_{\text{coh}, \text{Mn}}\).

### Table 2. Cohesive energy and the bond length of metal-phosphorus for metal doped phosphorene sheets.

| Doped metal | Sc  | Ti  | Cr  | Mn  | Fe  | Co  | Ni  |
|-------------|-----|-----|-----|-----|-----|-----|-----|
| \(r_{\text{M-P}, \text{zigzag}}(\text{Å})\) | 2.596 | 2.498 | 2.403 | 2.299 | 2.250 | 2.257 | 2.223 |
| \(r_{\text{M-P}, \text{armchair}}(\text{Å})\) | 2.501 | 2.383 | 2.357 | 2.235 | 2.231 | 2.227 | 2.201 |
| \(E_{\text{coh}}(\text{eV})\) | −2.88 | −2.87 | −0.42 | 0.99 | −1.22 | −1.56 | −1.35 |

### Thiophene adsorption on the metal doped phosphorene

The thiophene molecule approached the metal doped phosphorene plate in different configurations and their optimized structures were obtained. Calculating the adsorption energies of those structures shows that the most stable configuration is related to the thiophene molecule placing parallel to the phosphorene plate. Figure 6 shows the most stable thiophene adsorption configuration for each of the phosphorene doped sheets. As shown in figure 6, the best adsorption configuration in Cr, Mn, Fe, Co, and Ni doped sheets is the resultant of the interaction between the doped metal and the sulfur atom, while in the case of Ti and Sc doped sheets, the most stable configuration is the resultant of the interaction between the metal and the thiophene ring.

As shown in table 3, the adsorption energy \(E_{\text{ads}}\) order is found to be:

\[
E_{\text{ads,Sc}} > E_{\text{ads,Co}} > E_{\text{ads,Mn}} \approx E_{\text{ads,Fe}} > E_{\text{ads,Cr}} \approx E_{\text{ads,Ni}} \approx E_{\text{ads,Co}},
\]

whose values are \(-1.39, -1.33, -1.13, -1.12, -0.99, -0.98, -0.96\) eV respectively. The maximum adsorption energy corresponds to the Sc and Ti doped phosphorene. The adsorption energies of the phosphorene doped plate with all these metals are between \(-0.89\) and \(-1.33\) eV which are better adsorbent than the pure phosphorene. The minimum distances of the thiophene from the metal doped plates \(d_{\text{min}}\) are between 2.136 Å to 2.594 Å which are less than distances of the thiophene from the pristine phosphorene plate. After the adsorption of thiophene on the sheets, a slight increase in the bond length of sulfur-carbon \(r_{\text{S-C}}\) was also observed. This increase is due to the interaction between sulfur and the metal and weakening of the S–C bond. Figure 7 shows the diagram of increase in the S–C bond length in the adsorbed thiophene on metal doped phosphorene. Due to the highest adsorption energies, we expected that the greatest increases in \(r_{\text{S-C}}\) must be in thiophene adsorbed on Sc and Ti doped sheets but the interaction of thiophene is not directly related to the sulfur-metal atoms. So the least increases are observed for these two structures.

As shown in table 3, \(r_{\text{M-P}, \text{armchair}}\) has increased and the bond has been weakened in the armchair direction because of the interaction between the metal and the thiophene molecule. The changes in \(r_{\text{M-P}, \text{zigzag}}(\Delta r_{\text{M-P}, \text{zigzag}})\) are not regular.

Analysis of the Mulliken population of the doped phosphorene plates after thiophene adsorption has been represented in table 4. The results indicate that the charge transfer is from the thiophene molecule to the plate.
Figure 6. The most stable configuration of thiophene adsorption on (a) Sc, (b) Ti, (c) Cr, (d) Mn, (e) Fe, (f) Co, (g) Ni doped phosphorene.

Table 3. Adsorption energy, minimum distance between thiophene and metal doped phosphorene sheet, and the changes in M–P and S–C bond length.

| Doped metal | Sc  | Ti  | Cr  | Mn  | Fe  | Co  | Ni  |
|-------------|-----|-----|-----|-----|-----|-----|-----|
| $E_{\text{ads}}$ (eV) | $-1.39$ | $-1.33$ | $-0.99$ | $-1.13$ | $-1.12$ | $-0.96$ | $-0.98$ |
| $d_{\text{min}}$ (Å) | 2.136 | 2.153 | 2.594 | 2.278 | 2.371 | 2.472 | 2.447 |
| $\Delta r_{(M-P)_{\text{armchair}}}$ (Å) | $+0.089$ | $+0.038$ | $+0.022$ | $+0.023+$ | $+0.003$ | $+0.030$ | $+0.028$ |
| $\Delta r_{(M-P)_{\text{zigzag}}}$ (Å) | $-0.004$ | $+0.024$ | $+0.030$ | $-0.003$ | $-0.026$ | $+0.064$ | $+0.038$ |
| $\Delta r_{(S-C)}$ (Å) | $+0.012$ | $+0.014$ | $+0.019$ | $+0.025$ | $+0.016$ | $+0.017$ | $+0.016$ |

Figure 7. Increase of $r_{(S-C)}$ in the adsorbed thiophene on metal doped phosphorene.
and the greatest values are for the Sc and Ti doped phosphorene which is in agreement with the adsorption energy results.

For further investigation, the PDOS of the metal dopants before and after the adsorption (in complex) and the PDOS of sulfur atom of the thiophene after the adsorption were plotted in figure 8. In these diagrams, the d orbitals of the intermediate metals have changed after the thiophene adsorption and the peak of d orbitals have grown slightly and moved to the left in the range of 0 to $-6 \text{ eV}$. These changes are quite visible in Cr, Mn, Fe, Co and Ni doped diagrams, representing the electron transfer to the d orbitals of the metal. The overlap of the p orbitals of sulfur with d orbitals of the metal in the range of $-2$ to $-6 \text{ eV}$ can be the reason for these changes. On the other hand, the overlap of the d orbitals of Sc and Ti with the p orbitals of sulfur is less than that of the previous metals, which indicates the interaction of the thiophene results from the ring.

The isosurface of the electron density difference of thiophene adsorption on pristine phosphorene and also on metal doped phosphorene has been represented in figure 9 (isosurface value: 0.03 electrons/Å³). The blue

| Phosphorene-M doped | Sc  | Ti  | Cr  | Mn  | Fe  | Co  | Ni  |
|---------------------|-----|-----|-----|-----|-----|-----|-----|
| Sheet's partial charge after adsorption | $-0.388$ | $-0.358$ | $-0.253$ | $-0.279$ | $-0.226$ | $-0.252$ | $-0.192$ |

Figure 8. PDOS of metal dopants and sulfur atom of thiophene.
region shows the accumulation of the electrons and the yellow region shows electron depletion. With regard to phosphorene doped with $M=\text{Cr, Mn, Fe, Cr and Ni}$, electron transfer is between sulfur and the metal, while for $M=\text{Sc and Ti}$, the interaction is found to be between the thiophene ring and the dopant metal. In the case of pristine phosphorene, the interaction is weak.

Conclusions

In this paper, the adsorption of thiophene on the surface of pure and metal doped ($M=\text{Sc, Ti, Cr, Mn, Fe, Co and Ni}$) phosphorene was investigated. The adsorption energy of thiophene on the pure phosphorene in the best configuration was found to be $-0.50$ eV. After doping these metals, the interaction became stronger and the adsorption energy increased. The order of the adsorption energies is:

$E_{\text{ads,Sc}} > E_{\text{ads,Ti}} > E_{\text{ads,Mn}} \approx E_{\text{ads,Fe}} \approx E_{\text{ads,Cr}} \approx E_{\text{ads,Ni}} \approx E_{\text{ads,Co}}$, whose values are $-1.39$, $-1.33$, $-1.13$, $-1.12$, $-0.99$, $-0.98$, $-0.96$ eV respectively. The results of Mulliken population analysis revealed that the electron was transferred from the thiophene molecule to the phosphorene plate. PDOS curves and the images of electron density difference were obtained for further study. In the case of phosphorene doped sheet (where $M=\text{Cr, Mn, Fe, Co and Ni}$) the interaction occurs between the sulfur atom and the dopant metal; however, in the case of $M=\text{Sc and Ti}$, the interactions found to be between the ring and the dopant metal. The results show that phosphorene doped with transition metal could be suggested as an adsorbent of thiophene and it is more preferable than pristine phosphorene.

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