

# Interaction of CO with an hBN surface doped with Ti and Pt: A First Principles Study

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**Abstract.** We studied the possible catalytic effect that a transition metal atom could have after being adsorbed in a surface of hexagonal boron nitride (hBN). We considered platinum and titanium, performing *ab-initio* calculations, including molecular dynamics at 300K, within the Density Functional Theory. We considered an hBN surface either with a vacancy of a Boron atom, or with a vacancy of a Nitrogen atom, and we found that both titanium and platinum are absorbed at the place of the vacancy for both cases considered. Afterwards, we found that this decoration of the hBN surface indeed has a catalytic effect on the adsorption of a carbon monoxide molecule. Possible desorption was explored, at 800 K. To perform the calculations, the Quantum ESPRESSO package code was used. The generalized gradient corrected Perdew-Burke-Ernzerhof (PBE) approximation was used for the exchange and correlation functional.

## 1. Introduction

The study and development of surfaces that can absorb air pollutants is of a continuous interest in our society. In particular, carbon monoxide (CO) is a very poisonous gas even at levels of only 0.1% (1000 ppm), and a prolonged exposure can cause death in minutes [1,2]. Various materials, like graphene, have been studied to find ways of absorbing or detecting CO from the air [3,4].

Among those different materials, Boron nitride may be of particular interest, because of its availability and properties. Boron nitride has a structure similar to that of graphene and carbon nanotubes, for instance, Hexagonal boron nitride (hBN) has the same atomic structure than graphene, only with a lattice constant 1.8% bigger than the latter. hBN is also an electrical insulator [5], which can be useful when the electrical conductivity of graphene is undesirable.

Several *ab-initio* studies have been made on the CO adsorption in BN surfaces. Some have considered the BN sheet with no vacancies, with Stone-Wales defects, or with doping of different atoms, like Aluminum [6]. The interaction between CO and BN-based fullerenes has also been studied [7].

In this work, we considered an hBN surface with a vacancy of either a Nitrogen or a Boron atom. In each case, we studied its interaction with a CO molecule and then we considered the case when the vacancies are filled with a platinum atom and with a titanium atom. A good understanding of the mechanisms of adsorption for these pollutant molecules is relevant in the search of surfaces that can be used as sensors or cleaning devices of air and water.

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## 2. Method

*Ab-initio* molecular dynamics calculations were made, at 300K, based on the Density functional Theory (DFT) [8]. The Quantum ESPRESSO package code was used, this package considers a plane-wave expansion for the electronic wave functions, and periodic boundary conditions [9]. The generalized gradient corrected Perdew-Burke-Ernzerhof (PBE) approximation [10] was considered for the exchange and correlation functional. When considered appropriate, some of the calculations were repeated by using the van der Waals functional vdW-DF2 of Lee et al. [11]

The pseudo potentials are norm-conserving Troullier-Martins [12] in the Kleinman-Bylander fully separable form [13]. All calculations are non-relativistic and without polarized spin. The temperature is controlled via velocity rescaling and the adsorption energy is calculated according to the following definition:

$$E_{ads} = E_{system1+system2} - E_{system1} - E_{system2} \quad (1)$$

We considered an adsorption with energy equal or lower than 0.100 eV as physisorption, while any higher energy can be considered as chemisorption. The XCrySDen package was used for crystal structure visualization [14].

## 3. Results and Discussion

The first case we considered was that of the hBN surface with a vacancy of a Boron atom, or a vacancy of a Nitrogen atom. The MD calculations showed that in both cases, the CO molecule remains unaffected by the hBN surface. There is no adsorption in either case. To include the van der Waals interactions, we repeated the calculations with the vdW-DF2 density functional, and the results were similar, with no adsorption between the CO molecule and the hBN surface with the aforementioned vacancies.

We next considered a platinum atom, and the MD calculation showed that it was strongly absorbed in place of a nitrogen atom and also in place of a boron atom. In both cases, the adsorption energies of the platinum atom in the vacancy are similar (see Table 1). Subsequently we explored the interaction of a CO molecule with the two resulting Pt-doped hBN surfaces. In both cases, the CO molecule is chemisorbed by the platinum atom at the surfaces (Figure 1), with a higher adsorption energy in the case of the platinum in place of a boron atom (see Table 3).

Finally, we considered the catalytic effect of a titanium atom, which –as in the case of the Pt atom– was well absorbed into either a boron vacancy or a nitrogen vacancy (Figure 2). Unlike the platinum adsorption, however, we found that the titanium atom is more strongly absorbed into a boron vacancy than it is into a nitrogen vacancy, with the adsorption energy of the former case being more than three times larger than the one of the latter case (see Table 2). We then found that the CO molecule can be chemisorbed by the titanium atom when the former is either at the boron vacancy or at the nitrogen vacancy (see Table 3).

Our results are consistent with the fact that the hBN surface is usually considered as chemically stable when pristine, but the addition of either the Ti or Pt atoms, facilitates the charge exchange between any of those two and the CO molecule, resulting in adsorption.

We explored the possibility of desorption by performing MD calculations of the four cases of a chemisorbed CO molecule, at 800 K. We found that, at such temperature, the CO remains absorbed into the surface. We could then consider that the CO is chemisorbed by the catalysts, and that the hBN surface acts as a substrate.

**Table 1.** Energies of adsorption,  $E_{\text{ads}}$ , (in eV) of Pt into the hBN surface, for the two cases considered.

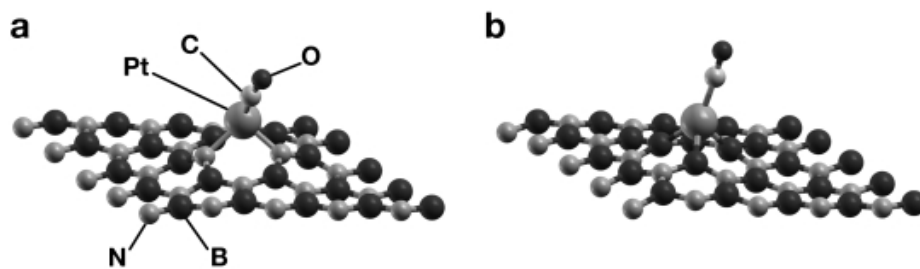
Surface	$E_{\text{ads}}$	Type of adsorption
hBN with a B vacancy	−6.926	chemisorption
hBN with an N vacancy	−6.813	chemisorption

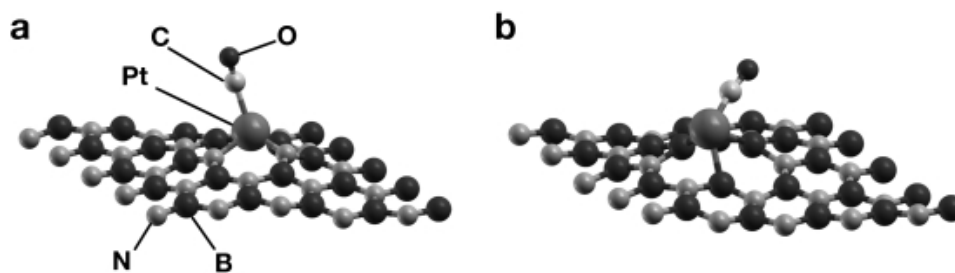
**Table 2.** Energies of adsorption,  $E_{\text{ads}}$ , (in eV) of Ti into the hBN surface, for the two cases considered.

Surface	$E_{\text{ads}}$	Type of adsorption
hBN with a B vacancy	−12.302	chemisorption
hBN with an N vacancy	−3.825	chemisorption

**Table 3.** Energies of adsorption,  $E_{\text{ads}}$ , (in eV) of the CO molecule into the hBN surface, for all cases considered.

Surface	$E_{\text{ads}}$	Type of adsorption
hBN with a B vacancy	---	No adsorption
hBN with an N vacancy	---	No adsorption
hBN with Pt in B vacancy	−2.106	chemisorption
hBN with Pt in N vacancy	−1.164	chemisorption
hBN with Ti in B vacancy	−1.530	chemisorption
hBN with Ti in N vacancy	−1.679	chemisorption

**Figure 1.** Final configurations for the interaction of a CO molecule atom and an hBN surface where a Pt atom has been previously absorbed in place of (a) a boron vacancy and (b) a nitrogen vacancy. In both cases, the CO molecule is chemisorbed by the system, without being dissociated by it. The first case shows a higher value for the adsorption energy of the CO molecule.



**Figure 2.** Final configurations for the interaction of a CO molecule atom and an hBN surface where a Ti atom has been previously absorbed in place of (a) a boron vacancy and (b) a nitrogen vacancy. Here, the CO molecule is chemisorbed as well, and the energies of adsorption are similar in value.

#### 4. Conclusions

We found that the hBN surface has no relevant effect in the interaction with CO when pristine, or even when there are vacancies in the surface. The mechanism of adsorption may depend on the charge distribution due to either the platinum or titanium atoms. The catalytic effect of both the Pt and Ti atoms in the interaction between the hBN surface and the CO molecule can be due to their modification of such charge distribution.

Both the Ti and Pt atoms, while occupying vacancies of the hBN surfaces, can absorb the CO molecule in all cases considered. We found that the CO molecule is chemisorbed in the Pt-decorated hBN surface, with adsorption energies of  $-2.106$  eV (B vacancy) and  $-1.164$  eV (N vacancy). The CO molecule is also chemisorbed in the Ti-decorated hBN surface, with adsorption energies of  $-1.530$  eV (B vacancy) and  $-1.679$  eV (N vacancy). The fact that the substrate is a readily available material, such as hBN, instead of the bulk titanium or platinum surfaces, would be potentially useful in technological applications.

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