Adsorption of carbon monoxide, carbon dioxide and methane on hexagonal boron nitride with high titanium coverage

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ABSTRACT

We used density functional theory and molecular dynamics to explore the adsorption of CO, CO_2, and CH_4 on a layer of h-BN with high titanium coverage. After optimization, we found that each titanium atom is located above each of the hexagons of the surface. We considered atmospheric pressure and 300 K. It is found that the first molecule is adsorbed and dissociated on the surface. The CO_2 molecule is broken into O and CO. The methane molecule is physisorbed, and not dissociated. It is desorbed at 370 K.

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1. Introduction

Carbon monoxide, carbon dioxide and methane are environmental problems. CO is a toxic gas which, at normal conditions is tasteless, odorless, and colorless. It comes primarily from incomplete combustion of carbon containing fuels. It is not-irritating, and it is an asphyxiant. At high levels, it is deadly. The investigation of the adsorption of carbon monoxide on palladium and transition metals is an attractive research topic. There are theoretical and experimental studies on the adsorption of carbon monoxide on the Ti [001] surface [1–4].

On the other hand, many industrial processes around the world produce CO_2 and CH_4. These gases are two of the main greenhouse gases emitted today [5]. At the present, the removal of these gases from the atmosphere is mainly done using amine baths. This process presents several problems. Among them, we have additional processing and corrosion control [6]. Another procedure is by chemically capturing CO_2 using oxides [7]. However, to remove these greenhouse gases, adsorption processes have been considered too. Among the materials that have been studied for these processes, we have activated carbons, zeolites, and porous metal–organic frameworks [8,9].

In previous works, we studied the adsorption of these three gases on a titanium–graphene system with high metal coverage [10,11]. We found that the carbon monoxide molecule is adsorbed and dissociated on this surface [10]. The carbon dioxide molecule is adsorbed and dissociated into two parts: O and CO [11]. Finally, we obtained that the methane molecule adsorbs with no dissociation. It is physisorbed, and desorbs at 600 K [11].

In this work, we studied the adsorption of these gases considering a high titanium coverage over a different substrate. Here, the system we investigated is a layer of the hexagonal boron nitride with high titanium coverage (h-BNTi). The influence of the substrate may be important. Boron nitride is a synthetic material. It was discovered in the late nineteenth century. Boron and nitrogen being neighbors of carbon in the periodic table have atomic radii comparable to the latter. In its hexagonal form (h-BN), boron nitride has a crystal structure similar to that of graphite. This is the structure that we considered in this work, although boron nitride can also exhibit a cubic structure [12]. Currently, it is possible to prepare boron nitride nanotubes and sheets [13]. In particular, large-scale fabrication of h-BN nanosheets were reported [14]. These nanotubes and nanosheets can be used, among other applications, as a mechanical substrate for graphene. In addition, a BN nanosheet is a unique insulating two-dimensional system to explore [14–16].

The aim of this work is to provide new insights for the seeking of functionalization methods that could widen the application fields of boron nitride nanomaterials. In particular, we believe that the use of titanium atoms decorating the h-BN surface in the way that we propose, is preferable to working with the titanium surface alone for this type of applications, because the h-BN surface is lighter and could be potentially easier to work with, in a practical device. Previous studies have found that functionalized boron nitride surfaces could be suitable for electronic applications such as gas sensors [17].

2. Method

We performed density functional theory (DFT) calculations, with the local density approximation (LDA), and the general gradient

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approximation (GGA), molecular dynamics (MD), within the Born–Oppenheimer approximation with the Quantum Espresso code [18]. For exchange–correlation energies, we used the Perdew–Zunger expression [19], for LDA, and the Perdew–Burke–Ernzerhof (PBE) approximation for GGA [20]. We used the norm conserving Troullier–Martins pseudopotentials [21], in the fully separable form of Kleinman–Bylander [22].

We considered as valence electronic states for boron: $2s^2 2p^1$, for nitrogen: $2s^2 2p^3$, for hydrogen: 1 s, for carbon: $2s^2 2p^2$, for oxygen: $2s^2 2p^4$, for titanium: $3s^2 3p^6 3d^2 4s^2$. We performed non-relativistic, and non-spin polarized calculations. The cut-off energy was 1100 eV, and we took 40 k points within the Monkhorst–Pack special k point scheme [23]. The threshold energy convergence was 1.2×10^{-5} eV. For the validation of our pseudopotentials, we obtained by energy minimization in the CO_2 molecule, for the length of the C–O bond 1.193 Å and for the O–C–O angle, 179.9° (the experimental values are 1.163 Å and 180°, respectively [24]). In the same manner, with the hydrogen pseudopotential we obtained for the H–C chemical bond length in CH_4 1.097 Å and for the H–C–H angle 109.36° (the experimental values are 1.087 Å and 109.4°, respectively [24]).

In the same way, and using the pseudopotential for titanium, we obtained for the lattice parameter $a = 2.863$ Å and for c 4.5444 Å, the experimental values are 2.950 and 4.683 Å, respectively [24]. In the case of h-BN we obtained for the B–N chemical bond length 1.447 Å, and for the lattice parameter c 6.661 Å; the corresponding experimental values are 1.446 Å, and 6.661 Å, respectively [24].

We represented the system h-BNTi using a hexagonal unit cell with $a = b = 5.0$ Å and $c = 40$ Å, with periodic conditions, containing four Ti atoms, four B atoms, and four N atoms (see Fig. 1). In the c direction, we took a large enough separation to ensure that there is no interaction between adjacent Ti and h-BN sheets.

We used at MD 300 K and the definition for the adsorption energy $\Delta E = E(h\text{-}BN + Ti) - [E(h\text{-}BN) + E(Ti)]$; where $E(h\text{-}BN + Ti)$ is the energy of the final optimized configuration; $[E(h\text{-}BN) + E(Ti)]$ is the energy of the initial system, which is h-BN alone plus the energy of Ti alone with no interaction between them. We found that the adsorption energy is -6.12 eV/Ti with LDA, and -6.16 with GGA. The Ti atoms are contained in two different planes.

This configuration is similar, not exactly equal to that of Ti–graphene with high metal coverage (C_2Ti) [11]. In the following, and in order to compare these two systems, we describe some parameters of the optimized h-BNTi system, and we write in a parenthesis the corresponding value of the parameter of the optimized C_2Ti system.

The Ti atoms are contained in two different planes. The nearest Ti atom to the h-BN plane is at 2.965 (1.828) Å. The other plane of titanium atoms is at a distance of 4.14 (3.239) Å from the h-BN (graphene) plane. In this way, the distance from the titanium lower plane to the titanium upper plane is 1.176 (2.815) Å. The distance Ti–Ti is 2.89 (4.22) Å and 2.418 (2.44) Å on the upper plane and on the lower plane, respectively, see Fig. 1a. From a Lowdin charge analysis, we found that the Ti atoms of the upper plane are positive, with a charge +0.413 (+0.335), and the Ti
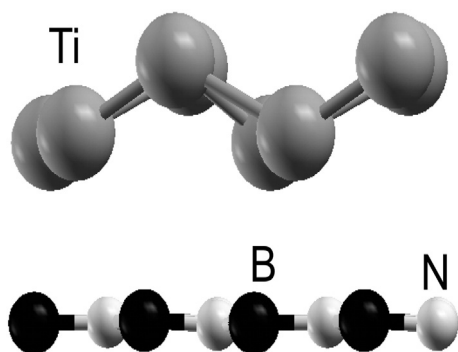
atoms of the lower plane are negative with a charge −0.350 (positive with a charge +0.548). Clearly, there are different charge transfers between the titanium layer and the substrates.

The origin of the different charge distributions on the titanium atoms within the titanium layers can be seen, in a simple fashion, on the distinct values for the electronegativity of the atoms on each substrate. The corresponding values of the Allen electronegativity in Pauling scale are 2.051 for boron, 3.066 for nitrogen, and 2.544 for carbon. It is convenient to mention that the Pauling electronegativities are very close to these values.

Clearly, the two titanium surfaces should not have identical properties. In this way, these two surfaces of titanium with a different substrate should not interact in exactly the same way with a given molecule or atom.

Certainly, for the h-BnTi configuration, we still have a hexagonal distribution of Ti atoms after optimization. Each Ti is above a hexagon. On the other hand, it is well known that the Ti[001] surface is hexagonal, with the atoms on one plane, and a Ti–Ti distance of 2.95 Å [24]. In this way, the surface for our system h-BN–Ti resembles the Ti[001] surface. In Figs. 1(a), 2(a), and (3) we show this surface. Notice that the two surfaces are not identical.

After the h-BNTi surface was optimized, we investigated its interaction with CO, CO_2, and CH_4. We defined the adsorption energy of each molecule, M: $\Delta E = E(h\text{-}BNTi + M) - [E(h\text{-}BNTi) + E(M)]$; where $E(h\text{-}BNTi + M)$ is the energy of the final configuration; $[E(h\text{-}BNTi) + E(M)]$ is the energy of the original system, which is the energy of the h-BNTi solely with no interaction with M, plus the energy of the molecule alone. For each molecule, we considered different initial possible orientations with respect to the h-BNTi surface. 300 K and atmospheric pressure were considered in our calculations. We controlled the temperature in the MD calculations via velocity rescaling. The pressure in the Quantum espresso code was controlled via a variable super cell size. The Parrinello–Raman barostat is used. The zero pressure corresponds to atmospheric pressure. We describe our results in the following.

3. Results and discussion

3.1. Adsorption of the CO molecule

We found that the carbon monoxide molecule is always chemisorbed and dissociated on the surface at 300 K.

We considered three initial orientations of this molecule to study its adsorption on the h-BNTi system. The first one was with the molecule line parallel to the adsorption surface; the second one was with the molecule line perpendicular to the surface, with the oxygen atom facing

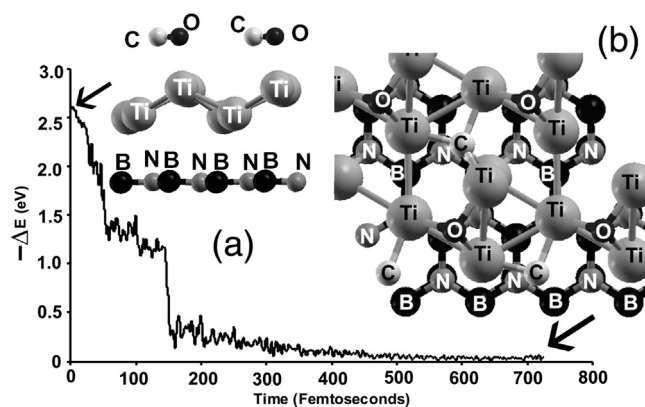Fig. 1. Unit cell oh h-BN with high Ti coverage (h-BNTi), after optimization.

Fig. 2. Time evolution of the interaction of a carbon monoxide molecule, for the first orientation we considered, with the h-BN surface. The unit cell of the initial configuration of the system is shown in (a). In the (b), we show the resulting surface composition. We considered 300 K and atmospheric pressure.