A NOVEL GRAPHENE SYSTEM TO ADSORB GAS POLLULANTS CO_2 AND CH_4

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Abstract

We have found that coating the graphene monolayer with Ti atoms to form the C_2Ti system, molecules such as carbon dioxide and methane, are adsorbed on the coated graphene. Previously, the adsorption of other gases on a graphene layer has been studied. In this work, it is proposed and probed with success that adding Ti atoms to the graphene layer, we obtained a useful and cheap system to adsorb and capture some of the most dangerous and pollutant gases such as CO_2 and CH_4. Using density functional theory and molecular dynamics, we obtained that the planar orientation of one CO_2 molecule above the C_2Ti system, is the most favorable one. After this final configuration was obtained, we achieved the saturation of the system when a second CO_2 molecule was added. In this case, we obtained 23.43 wt % for carbon dioxide. We also report in this work the density of states, the partial density of states, band structure, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) for the system. In a similar way, we studied the capacity of the C_2Ti system of adsorbing methane. The most favorable initial configuration was when three of the hydrogen atoms of the methane molecule are in a plane nearly close and parallel to the graphene layer. The methane molecule is adsorbed but not dissociated in the process. The adsorption energy is -0.176 eV. The C_2Ti system is saturated with 5.28 wt % for the methane gas. Finally, we obtained that the methane molecule is desorbed at 600 K.

Oral presentation

1. - Introduction

The world wide increase in the green house gases such as CO_2 and CH_4 has contributed in the necessity to design novel and not expensive materials that could be used to adsorb among others such a kind of pollutants. Carbon based materials have proven to adsorb hydrogen when they are coated with some atoms like Ti. The main objective in this work is to propose a novel material and optimizing the adsorption of some gases when the carbon atoms in a graphene layer are addressed with some Ti atoms. This is a Density Functional Study and is complemented by some molecular dynamics to take account of the temperature effects on the adsorption of gases such as carbon dioxide and methane, for example.

The novel material studied here is based on the graphene layer. The hexagonal arrangement of the carbon atoms on a graphene layer is above of Figure 1. Below we show the CO_2 and CH_4 molecules, respectively, above a portion of a graphene layer with 8 carbon atoms.

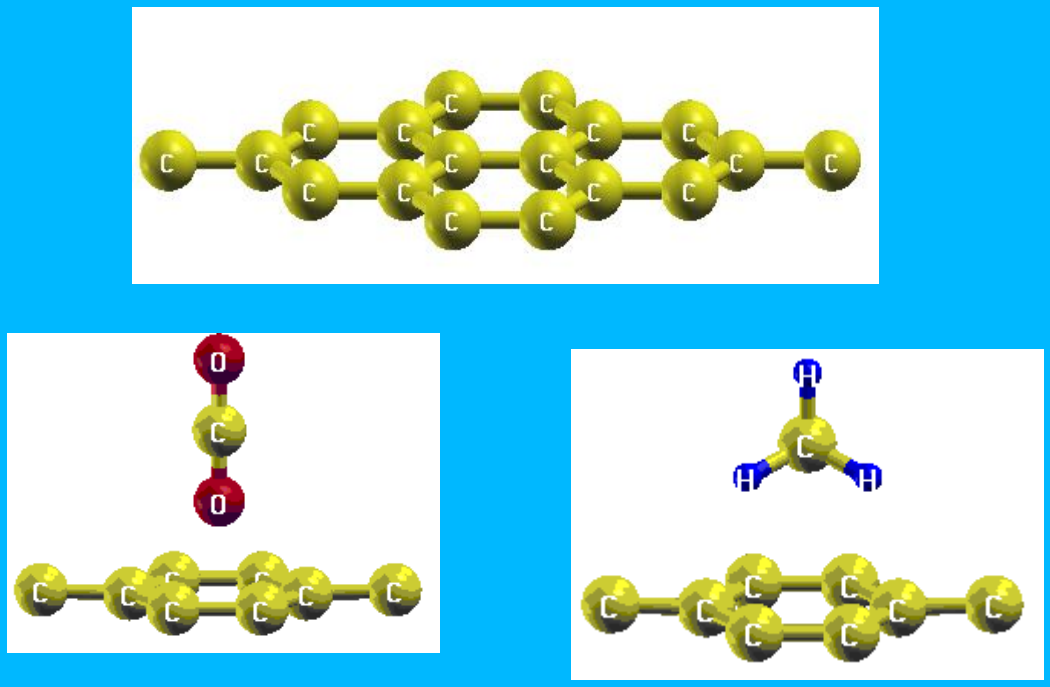

Figure1. Unit cell for the system C_2Ti.

2. – Method

First we study the stability of the pristine graphene. With a complete characterization of the initial system it is added only one Ti atom above the graphene layer and it is obtained additional information as the new energy of the system, the distance from the Ti atom to the graphene layer, for example. If instead of adding only one atom, it is placed a molecule as CO_2 or CH_4, much more information is obtained. Lengths, angles and relative orientation of each molecule above the graphene layer are obtained. A comparison is made also for the energy changes in the different studied systems. For all the computational calculations it was used the Quantum Espresso computer code. For the carbon atom it was used the Perdew-Zunger exchange correlation functional and the LDA (local density approximation) pseudopotential.

3.-Results and discussion

Minimizing the energy of the graphene layer, it was obtained 1.4076 Å for the C-C bond length. The experimental result is 1.415 Å. From a theoretical study [1] it was obtained that the CO molecule acts always as a donor giving a net charge to the graphene layer in the range 0.1 to 0.19 e. The adsorption energy was from 8.4 to 14.1 meV. The most favorable configuration was with the CO molecule parallel to the graphene layer above the C-C bond (14.0 meV) or above a carbon atom (14.1meV). It was obtained the distance 3.74 Å from the CO molecule to the graphene layer. In a similar way, the most favorable configuration, from a theoretical-experimental study [2] with B3LYP for the CO_2 molecule was when it was above the hexagonal ring of the carbon atoms of the graphene layer. The adsorption energy was 173.44 meV. Other group [3] make a TPD (temperature programmed desorption) study for the adsorption and desorption of CO and CO_2 in a graphite policrystal. In general, the adsorption process can be obtained at room temperature. The CO and CO_2 desorption is in the range 400 – 700 K, and 423 – 443 K, respectively. One experimental result [4] for the binding energy of methane and graphene is 170 meV, in agreement with previous results in the range 171.97 – 182.33 meV. In a theoretical study [5], they conclude that LDA and not GGA, gives good results to study the methane-graphene system. The experimental adsorption energy is 126 meV and the calculated are in

the interval 118 – 122 meV. The equilibrium distance from the C atom of the methane molecule to the graphene layer is 3.21 Å.

The system proposed here is denoted C_2Ti. It is a graphene layer coated with Ti. It is designed to operate at room temperature and ambient pressure, 1 atm. One advantage of the novel structure is besides its stability, the C-Ti strong bond. To optimize the geometry a cut off energy of 1100 eV was used and 40 points in the Monkhorst-Pack scheme. The total energies were converged to 10^{-6} eV. The unit cell for the system is on figure 2. It contains 8 carbon atoms and 4 Ti atoms. The hexagonal unit cell is given by a = b = 4.875 Å (2x2), c = 20 Å, with periodic boundary conditions along the z axis. The great value for the c parameter is to simulate an isolated system in that direction.

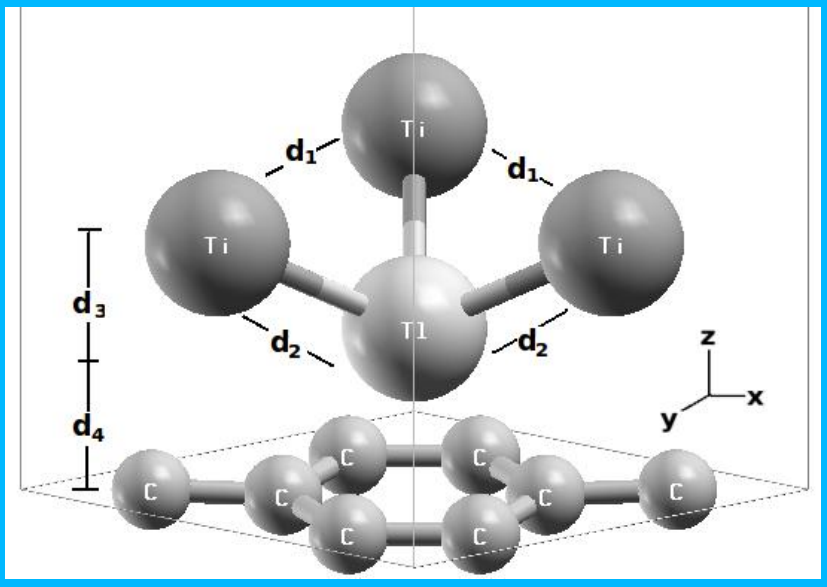

Figure 2. Unit cell for the system C_2Ti.

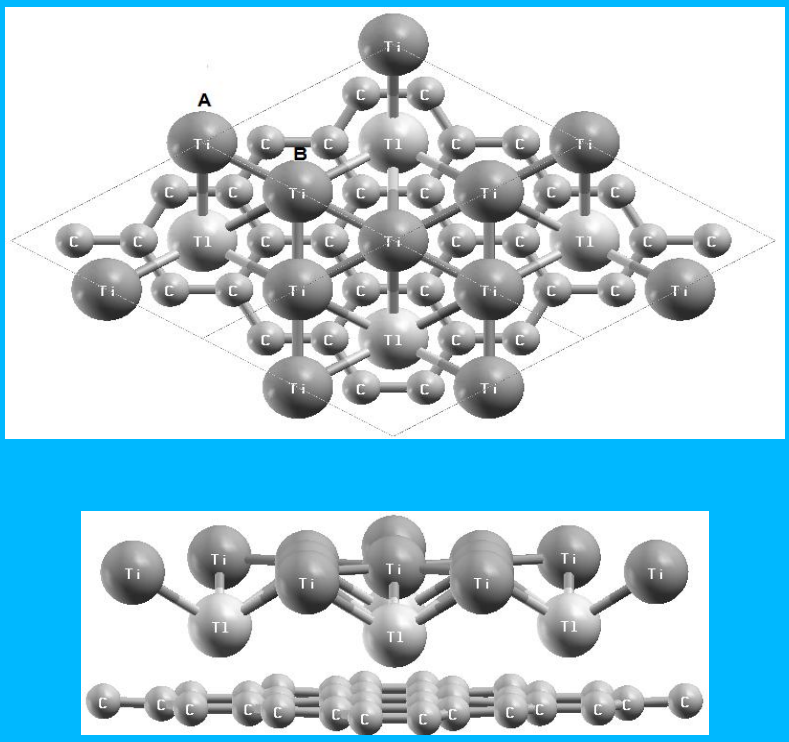

Figure 3. Periodicity of the system C_2Ti. The light Ti atoms are closer to the carbon atoms.

The distance between the Ti planes is d_3 = 1.42 Å. The distance from the graphene plane to the closer Ti plane is d_4 = 1.83 Å. The distance Ti-Ti is d_5 = 4.219 Å. The Löwding charge analysis says that 75% of the carbon atoms has a net charge of -0.039 e and the remaining 25% a charge of + 0.011 e. Ti atoms closer to the graphene layer have a charge of + 0.548 e. The other Ti atoms have a net charge of + 0.335 e. The band structure of the C_2Ti system is very different from the corresponding to the graphene layer. The new system is a good conductor with a high density of states at the Fermi level. The graphene layer has been decorated with Ti atoms with adsorption energy of -1.67 eV. The 3d orbitals of Ti atom are very important for the binding and the transferred electrons from Ti atoms to the graphene layer. Once the C_2Ti system was characterized the adsorption of CO_2 and methane was studied. Molecular dynamics (MD) for temperature 300 K and atmospheric pressure were done for the systems. Their evolution was followed along 1000 time steps, each one of 0.9676 femtoseconds. The adsorption energy is calculated with the next formula

$$\Delta E = E(graphene+Ti+molecule) - E(graphene+Ti) - E(molecule) \quad (1)$$

A negative value of ΔE means adsorption of the system.

3a. $C_2Ti + CO_2$ system

A CO_2 molecule with different initial orientations was added to the C_2Ti system. The most favorable configuration for the adsorption is with the molecule parallel to the graphene plane. The initial distance from the C atom of the CO_2 molecule to the C atom of the graphene layer was 7 Å.

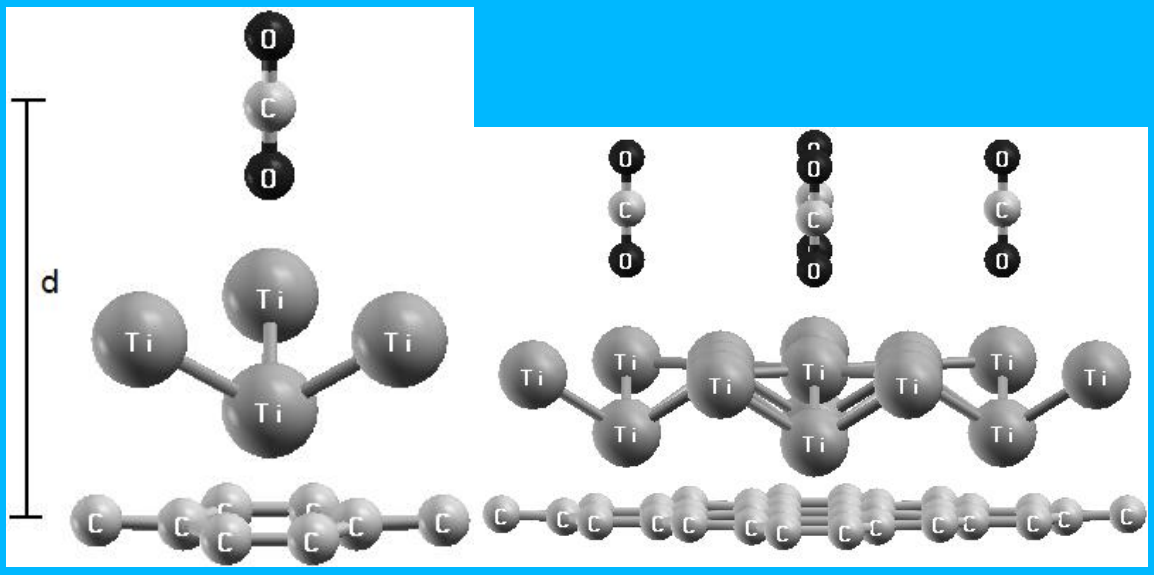

Figure 4. Initial configuration of the TiC_2 + CO_2 system in unit cell and periodic system.

Minimizing the energy the length of the C-O bond was 1.193 Å and the angle (O-C-C) was 179.9 degrees. The experimental values are 1.163 Å and 180 degrees. The final charge on the oxygen atoms is -0.348 e and +0.696 e for the carbon atom. Finally the CO_2 molecule is dissociated in one O atom and one CO molecule, which is adsorbed on the surface, with the C atom bonding to three Ti atoms. The O atom makes bond with the fourth Ti atom. The adsorption energy for the CO_2 molecule is - 4.96 eV. The distance of the O atom to the Ti atoms are 2.02, 2.08, 2.03 and 1.82 Å, respectively. The final distance for the CO bonding is 1.32 Å. The distances C-Ti are 2.27, 2,22 and 2.10 Å, respectively. The angle Ti-(CO) is 88.37 degrees.

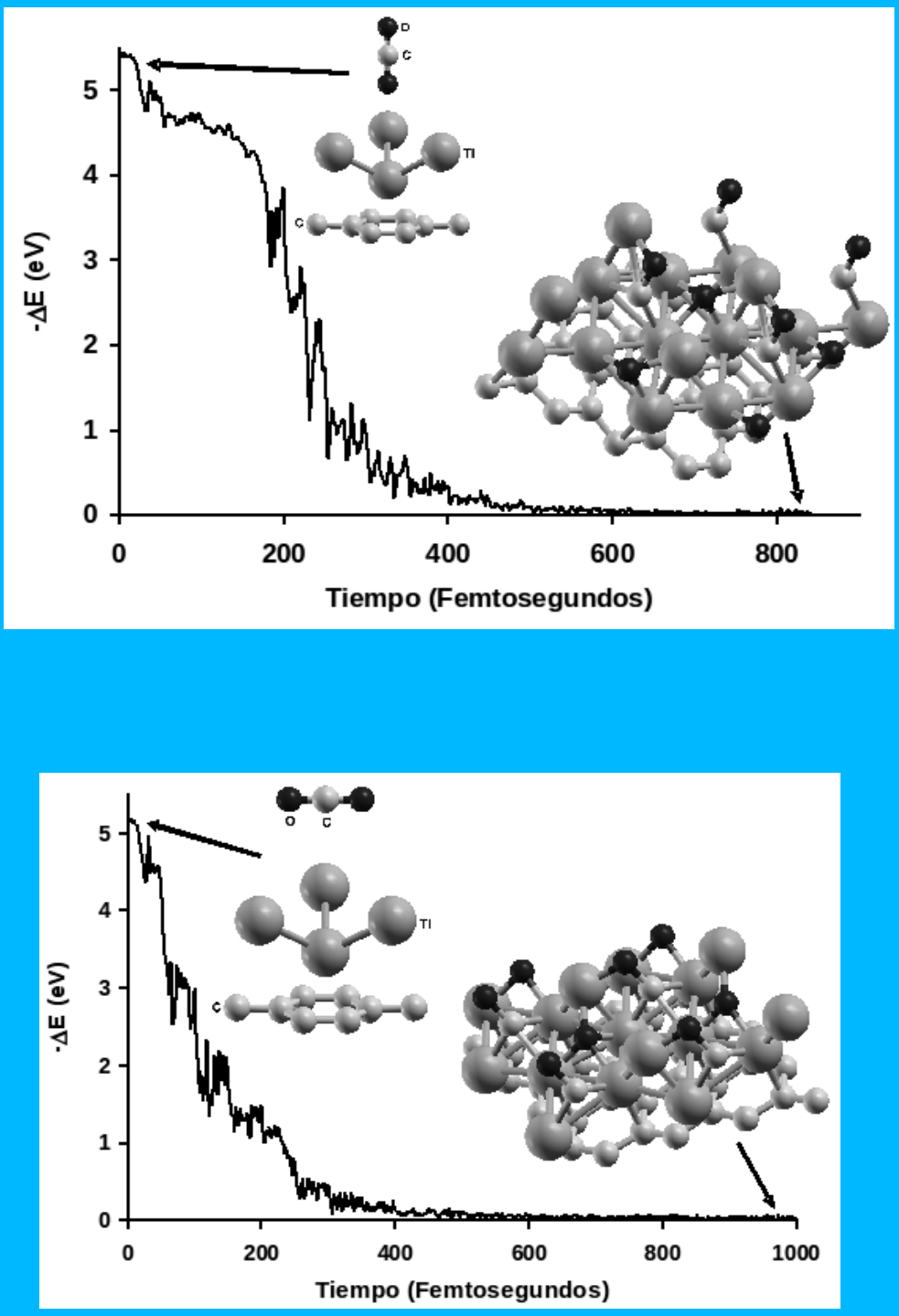

Figure 5. Molecular dynamics initial and final configuration for the interaction of the CO_2 molecule with the TiC_2 system. The initial orientation for the CO_2 molecule is perpendicular (parallel) to the graphene layer in the first (second) panel of the figure.

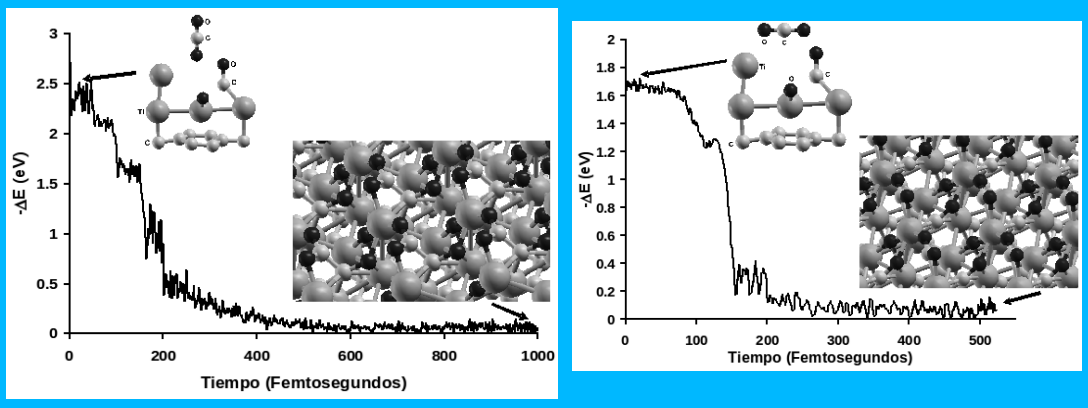

Figure 6. Molecular dynamics initial and final configuration for the saturation with two CO_2 molecules of the C_2Ti system. The initial orientation for the CO_2 molecule is perpendicular (parallel) to the graphene layer in the first (second) panel of the figure.

The density of states shows the Fermi level at 0.2523 eV. The metallic character of the C_2Ti system is reduced with the adsorption of the CO_2 molecule. This is explained with the reduction of the number of density of states at the Fermi level. The C_2Ti system is saturated when a second CO_2 molecule is adsorbed. Then is reached 23.43 wt %. After the adsorption of the first CO_2 molecule and the dissociation in one O atom and a CO molecule, we add a second CO_2 molecule initially in a perpendicular or parallel orientation respect to the graphene plane. The second CO_2 molecule is adsorbed with energy of -1.9 eV. The calculated density of states shows the Fermi level at 3.2410 eV. The metallic character of the C_2Ti system is reduced again with the adsorption of the second CO_2 molecule.

3b. $C_2Ti + CH_4$ system

The methane is a gas at normal pressure and temperature. It constitutes almost 97 % of the natural gas. The methane has a global warming potential of 23. This means that along 100 years each Kg of methane warms the Earth 23 more times than the same quantity of CO_2 gas. Because there are around 220 more times of CO_2 than methane in the earth's atmosphere, the contamination potential of methane has been neglected many times. With

the LDA pseudopoentials for C and H atoms it was obtained 1.097 Å for the equilibrium H-C bond length, and an angle H-C-H of 109.36 degrees for methane. The experimental values are respectively 1.0870 Å and 109.4 degrees. From Löwdin charge analysis it was obtained a net charge for the C atom of – 0.663 e, three of the H atoms have a positive net charge of 0.333 e, the other H atom, a negative charge of -0.333e. Several positions for the methane molecule were considered. The most favorable was when three of the H atoms of the molecule are coplanar with the graphene plane. The remaining H atom is farer from the graphene plane than the hydrogen plane. The configuration is in Figure 7. Because the Ti atoms have positive net charge in the C_2Ti system, they induce dipolar moments on the methane molecules and are attracted by the Ti atoms. Adsorption is predicted for the system even at room temperature. The attractive force for the system C_2Ti is strong due to the induced charge by the dipolar interaction.

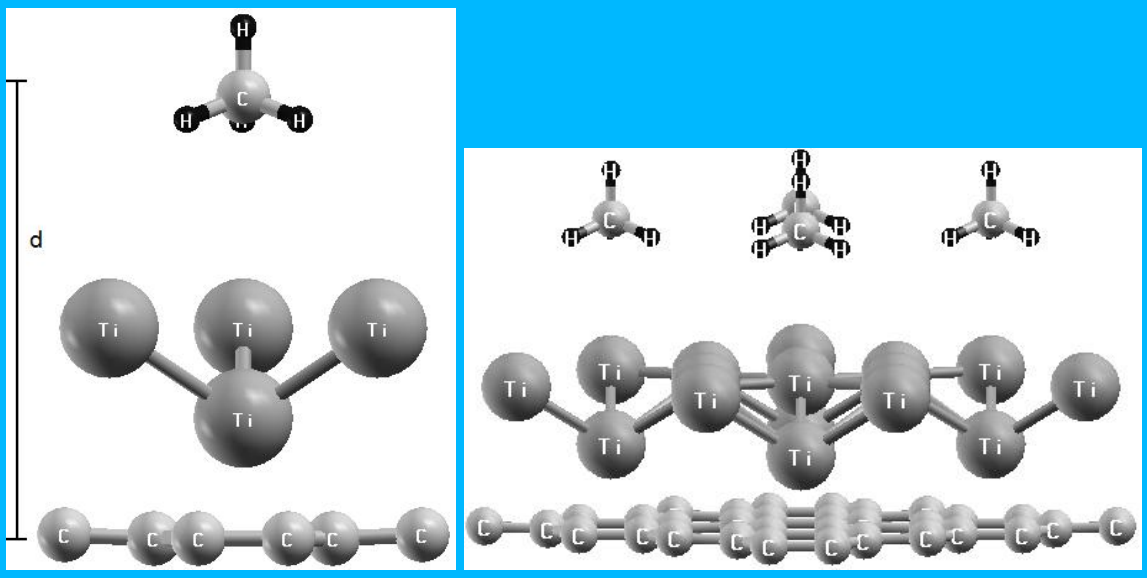

Figure 7. Initial configuration of the C_2Ti + CH_4 system in unit cell and periodic system.

The corresponding density of states and band structure calculation shows a high density of states at the Fermi level, which appears at 0.7013 eV. This means that the system C_2Ti with the methane molecule is still a good conductor. In the physisorption state the methane molecule polarizes slightly, the extra charge appears at the three hydrogen atoms closer to the Ti ion. There are also some small geometry changes. The change of – 0.05 Å for the

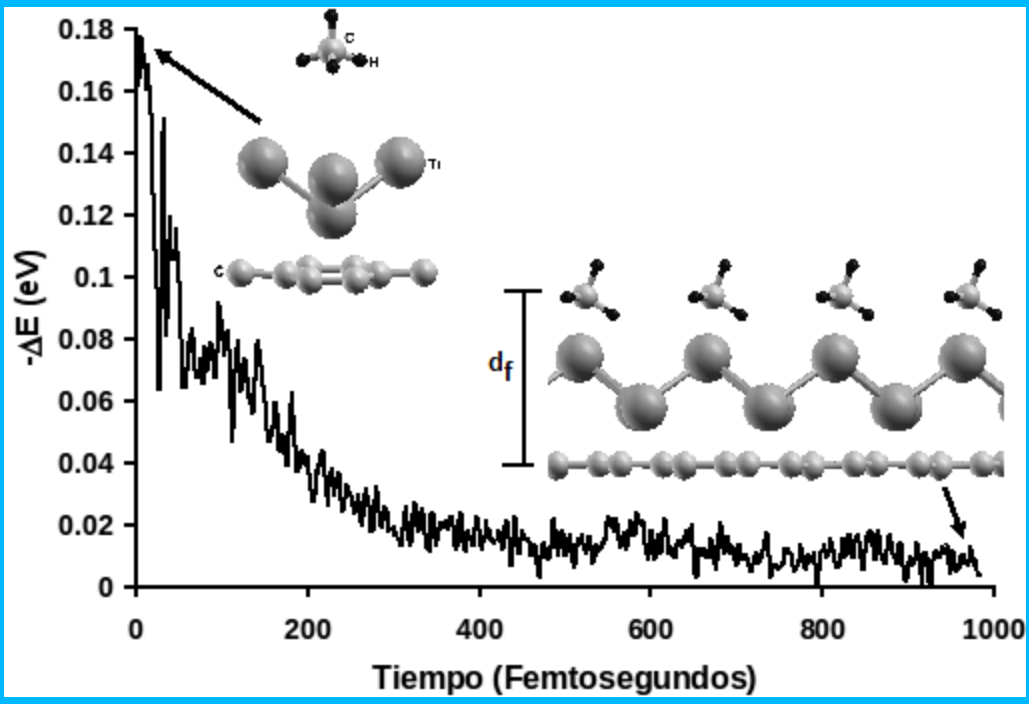

Figure 8. Molecular dynamics initial and final configuration for the interaction of the CH_4 molecule with the C_2Ti system.

distance graphene to the nearest Ti atom is an example of this. Physisorption makes some influence on the electronic structure of the system C_2Ti. Although the net charge for the Ti ions remains practically unchanged, there is a net charge transfer of 0.3 e to the methane molecule. In this case saturation is achieved with only one methane molecule with 5.28 wt % of methane. The desorption of the methane molecule is shown on Figure 9.

A comparison between the adsorption energies for the methane molecule on the surface [0 0 1] of Ti , with value -0.48 eV and on the C_2Ti system, with value -0.176 eV, makes easier the recover or capture of the methane molecule from the C_2Ti system, because the involved energy is smaller for the C_2 Ti system.

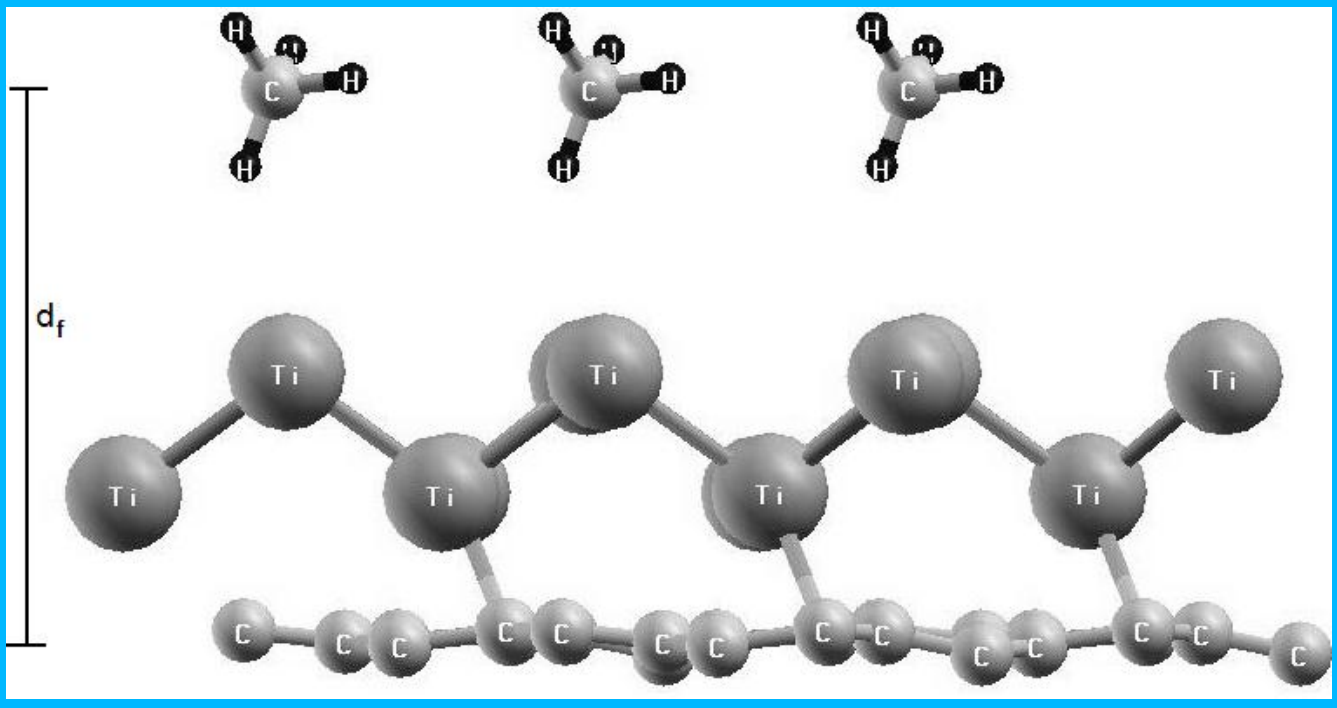

Figure 9. Configuration for the CH_4 molecule desorption at 600 K.
The distance d_f is 8 Å.

4. Conclusions

We have shown that a novel material named TiC_2, designed based on the graphene layer is a good material to adsorb some gases.

a.- The stability of the new system was obtained with computer simulation.

b.-The capacity of the new system C_2Ti to adsorb gases such as CO_2 and CH_4, has been demonstrated. The same has been obtained for other gases: CO and SH_4.

c. Due to the strong C-Ti interaction there is no Ti segregation when the graphene layer is covered with the metal.

d.- The system has the advantage over all other carbon materials of adsorbing several gases at room temperature.

e. - Its dissociciative power to transform dangerous molecules in other compounds has been illustrated in the case of the CO_2 molecule.

f. - The metal character of the system C_2Ti is preserved even to the saturation point.

g. - For the methane case, it is possible to recover the gas with warming the system to accessible temperatures.

h. - The feasibility of the system as a sensor is evident because of the changes on the density of states.

i.- The C_2Ti system maintain their adsorption-desorption properties. This is not the case for the Ti alone.

j.-The C_2Ti system is a cheap material based on C atoms.

k.- The charge transfer between the considered molecules and the C_2Ti system depends strongly on the molecule position respect to the Ti atom.

l.- The results help to understand better the adsorption properties of gases in carbon based structures, and those of catalytic elements that help to increase the adsorption process.

5. References

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