On the Interaction Energy among Propellant Components: A Carbon Black Model

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INTRODUCTION

The development of chemical propulsion, mainly by the increase of its efficiency has a central role in the progress of the aerospace propulsion in 21th century. Nowadays this development is possible, since the control of materials increased up to nanometric scale, allowing the synthesis of new propellants with superior performance and low environmental impact. From the quantum chemical point of view, there are three main characteristics to take in account in the development of propellants and its components: (1) Their energy content; (2) The chemical interaction among the components and; (3) The energy release in combustion and decomposition. In this work we are concerned about the chemical interaction between the fuel (paraffin) and the additive (carbon black) used in hybrid rocket propellants. Specifically, we constructed a model to describe the surface of carbon black and it`s interaction with weak adsorption systems (CH_4), in order to evaluate the capabilities of such model to describe interaction energies involved among propellant components.

METHODS

The Carbon black macromolecule is an agglomerated collection of carbon spheres, in which each sphere is made of graphitic carbon flakes that typically form broken concentric layers emanating from the core of the sphere[1]. We constructed a minimal model for the carbon black surface, consisting of two layers of a graphene fragment in a graphitic stacking geometry. Each layer has a mean diameter of 2 nm, representing the typical size of a carbon flake.

The three layers ONIOM methodology was employed to describe the model: The high and medium level layers consisted in DFT within M06-2X approximation with triple and double zeta basis sets, respectively, while in the low level layer a semi-empirical method was used. The high-level contained the 4 central rings and the considered molecule for adsorption (CH_4), while the mid-level contains all adjacent rings of the high layer, comprising 14 rings of the graphene outer layer. All other atoms and the entire inner layer are described with the low-level semi-empirical method.

RESULTS AND DISCUSSION

From the low-level semi-empirical methods considered (MNDO, PM3 and PM6), only PM6 presented an attractive stacking energy between the graphene layers, although with only 10% of the experimental value. Since the stacking energy does not vary significantly during the considered processes, this does not represent an issue for the model. The low-level should only represent a geometrical constraint, while the mid and high levels recover the largest part of the interaction energy. Figure 1 shows the calculated and experimental values of the distance and adsorption energy of methane over the flake surface.

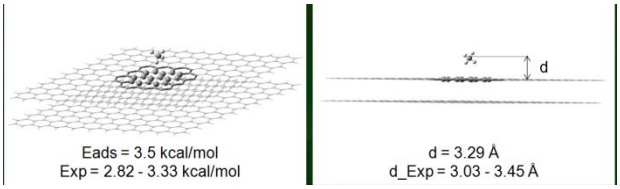

Figure 1. CH_4 adsorption on the CB flake model, obtained with DFT/Semi-empirical ONIOM methodology. Experimental values are given in reference[2].

CONCLUSIONS

The simulations performed in this work reveal the capability of the methodology to describe physical adsorptions, in agreement with the experiments,

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