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Study on the interaction of metallocene catalysts with the surface of carbon nanotubes and its influence on the catalytic properties. 1. Investigation of possible complex structures and the influence on structural and electronic properties

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ABSTRACT

The interaction of a single-walled carbon nanotube (SWCNT) with the Cp_2Zr^+-CH_3 has been studied with a hybrid quantum mechanics/molecular mechanics (QM/MM) method and density functional theory. At the first step, the QM/MM method has been validated by comparing its results with those of a related full QM approach. In this step, we used benzene, isobutane, and carboxyl species to model π···π, CH···π, and covalent interactions, respectively. According to our results, the QM/MM method is accurate enough to investigate covalent and noncovalent interactions with the surface of CNTs. After validating the method, the possible complex, i.e. Metallocene-CNT, structures have been investigated. We considered different π···π and CH···π configurations and found that: The Cp_2Zr^+-CH_3 can be attached to SWCNT via both π···π and C-H···π noncovalent interactions. The C-H···π configurations are more stable than the π···π analogues and those with the zirconium atom near the CNT surface are the most stable ones. We also examined the influence of the CNT on the electronic and steric properties of the metallocene. While the tube has a small effect on the electronic properties of the catalyst, it has a considerable impact on its steric environment, which may lead to the high molecular weight and tacticity products.

1. Introduction

Metallocene compounds as homogeneous single-site catalysts show a high catalytic activity for olefin polymerization. Composed of group IVB transition metals (Ti, Zr, and Hf), these catalytic systems allow a high degree of control on the polymer microstructure. For this reason, they are used extensively in the polymer industry and was the subject of numerous studies [1–4]. In a metallocene, the transition metal is sandwiched between aromatic rings which are called ancillary ligand. Usually, the ancillary ligands at the metal center are aromatic rings like cyclopentadienyl (Cp). The variation of ancillary ligands by the introduction of proper substituents or design new ligands changes the steric and electronic environment of the metal center. The environment of the metal center, both steric and electronic, governs the catalytic behavior of metallocene compounds and the various properties of produced polymers. In this respect, the development of new metallocene-based catalysts by the modification of ancillary ligands enables us to produce custom-designed and high-valued polymers, such as copolymers, functionalized polymers, and high molecular weight polymers [4–8].

Carbon nanotubes (CNTs) have interested many researchers because of their unique properties, such as mechanical strength, electrical conductivity, and optical activity [9–11]. This fascinating new class of materials is extremely promising for application in many areas of science. Because of its extraordinary properties, CNTs have many diverse applications in different fields of science and technology [12–14]. The properties of CNTs are governed by how graphitic sheets rolled up into a cylindrical shape. Depending on the arrangement of the hexagon rings along the tubular surface, CNT can have metallic or semiconducting properties [15].

The noncovalent wrapping of polymer chains around a CNT is a renowned phenomenon that impact the properties of both the CNT and the polymer chain [16–19]. Moreover, the metallocene compounds which are used in the synthesis of such polymers can interact with CNTs. The ancillary ligands of the metallocenes are

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aromatic compounds which can have different types of non-covalent interactions with CNTs. Such interactions can bind the metallocene catalyst to the CNT, and affect the catalytic properties of the metallocene compound. Park and co-workers studied metallocene based ethylene polymerization in the presence of multi-walled CNTs and reported that direct interactions between multi-walled CNTs and the Cp rings of Cp_2ZrCl_2 controlled polymerization behaviors, and led to the generation of polyethylene with an extremely high molecular weight [8].

In the case of metallocene catalysts, it is difficult to elucidate the relation between the catalytic properties and the catalyst structure due to the wide variety of circumstances. The nature and amount of the cocatalyst, combined with simultaneous steric and electronic effects of ligand framework, have a crucial influence on the catalytic process [20]. If one intends to investigate the influence of CNTs on the catalytic properties of metallocene compounds, the case is even more complicated because the CNT has interaction not only with the metallocene compound but also with the monomers and produced polyolefin chain [19]. A comprehensive inquiry of such influences needs proper consideration of both CNT-metallocene and CNT-olefin interactions simultaneously, and also the exploration of the polymerization mechanism in the presence of CNTs. However, in the first step it is essential to probe the nature and quality of interactions between CNTs and metallocene compounds.

As far as we know, there is no theoretical or experimental study on the interactions between metallocene catalysts and the surface of CNTs, therefore, we investigated the interactions between the surface of a SWCNT and a metallocene catalyst. For this propose, the methylated form of the simplest possible metallocene catalyst (Cp_2Zr^+-CH_3) was employed (Fig. 1). The specific CNT molecular structure considered in the present study are an 110-carbon metallic, (5,5), tube terminated with hydrogen atoms on both ends.

The results of this study are organized in the following way. Section 3.1 introduces the method which was used in this study and argues that this is a valid and efficient method for investigating interactions with the surface of CNTs; Section 3.2 investigates possible complex (Cp_2Zr^+-CH_3-CNT) structures and presents binding energies related to each structure; and Section 3.3 studies influence of the CNT on the structural and electronic properties of the metallocene, which can be helpful in predicting catalytic properties.

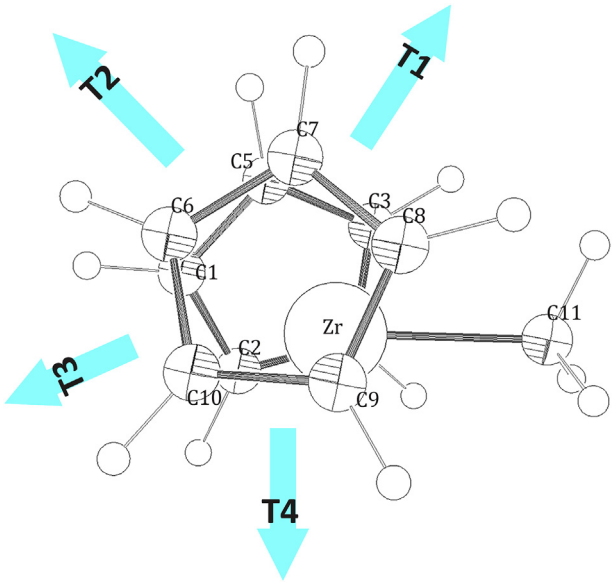

Fig. 1. The Structure of Cp_2Zr^+-CH_3. The arrows show the direction of the CNT surface in different T configurations.

2. Computational details

All of the calculations presented in this article was performed using NWChem 6.5 software package [21]. The software requires a preparation stage before the main QM/MM calculation, which creates topology and restart files. The original NWChem code has some difficulty to perform this preparation stage for CNTs, therefore, we made a minor code modification: The lines mbnd = nbnd + 3*nseq + 1 and mdih = ndih + 45*nseq + 1 in files src/argos/argos_prep_mktop.F and scr/prepar/pre_mktop.F have been converted to mbnd = nbnd + 6*nseq + 1 and mdih = ndih + 90*nseq + 1, respectively. In addition, before preparation stage, the links between segments must be explicitly defined in the PDB pdf file.

In the validation step of this study, The QM calculations, either as a part of the QM/MM calculations or as a pure QM ones, are based on DFT method and M06-2x level of theory [22] with the 6-31G(d,p) basis set. In contrast, in the main study, we used M06 hybrid meta exchange-correlation functional, which is recommended for application in organometallic chemistry and non-covalent interactions [22]. Moreover, we used the cc-pVDZ-PP [23] with Stuttgart-Koeln-mcdhf-rsc effective core potential [24] and the cc-pVDZ basis sets [25] for the description of the electronic configurations of zirconium and other atoms, respectively. The counterpoise method of Boys and Bernardi [26] and the D3 correction method of Grimme et al. [27] were used to account for basis set superposition error (BSSE) and dispersion forces, respectively.

For the description of intermolecular parameters in the MM region, the AMBER 99 force field [28] was employed and cut-off radius was set to 0.9 nm for all of the interactions. The QM/MM optimization follows a micro-iteration scheme where optimization of the QM and MM regions are alternated until self-consistency is reached [21]. The number of steps in each iteration was set to 9 and 99 for the QM and MM regions, respectively.

Finally, the NBO calculations performed by NBO 5 code [29] integrated into the NWChem code and the Mercury software [30] has been used to measure the geometrical parameters of the optimized structures.

3. Results and discussion

3.1. Method and validation

The surface of a CNT interacts with other compounds in two ways: (a) covalent attachment of chemical groups [16,31–36] (b) noncovalent adsorption or wrapping of various functional molecules [16,37–41]. Both covalent and noncovalent interactions on the surface of CNTs can be modeled properly by ab inito and DFT methods. But in the term of computational efforts, these methods have significant limitations. In the large basis set limit, ab inito and DFT methods formally scale as at least (M^4), M being the number of basis functions [42]. This scale makes vary cumbersome, if not impossible, to practice these methods on the systems as large as CNTs. In contrast, the computational cost of molecular mechanics (MM) methods, scales linearly for sufficiently large molecules [43]. “Molecular mechanics calculations may easily be performed on molecules comprising several thousand atoms” [43]. However, MM calculations reveal nothing about chemical bond breaking nor bond formation. Furthermore, MM methods work on the basis of force fields, which need to be parameterized. It means that MM methods need different parameters for different types of atoms and, therefore, are restricted by parameters.