Computational Materials Science 112 (2016) 92–95

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Magnetic and structural properties of single 3d transition metals adsorbed on corannulene: A density functional theory study

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ARTICLE INFO

Article history:
Received 15 May 2015
Received in revised form 18 September 2015
Accepted 15 October 2015
Available online 19 November 2015

Keywords:
DFT
Corannulene
Metallo-organic molecules
Spin–orbit interaction

ABSTRACT

We have obtained magnetic properties of single 3d transition metal atoms (from Sc to Ni) adsorbed on both concave and convex surfaces of corannulene. Binding energies, spin and orbital magnetic moments, and charge transfer between added transition metal and corannulene were determined. We have done our calculations in the framework of relativistic density functional theory in the regime of generalized gradient approximation. Our calculations show that TM atoms added on corannulene convex surface except Co and Ni are mostly stable on hollow site of hexagon rings, whereas for concave surface all TM atoms are stable on hollow sites of central pentagon ring except Sc where it is stable on C–C bond of pentagon ring. Binding energy calculations show that most TM atoms prefer to bind on the convex surface of corannulene. All structures are magnetized except Ni-corannulene structure.

1. Introduction

Molecular magnetism is a new research area consisting organic and metallo-organic materials with the aim of design, synthesis and investigation of the magnetic properties of molecular materials. These nanomaterials have potential applications for spintronic nano-devices [1–3]. Using organic materials, organic spintronic is trying to mediate or control a spin-polarized signal [4,5]. Moreover 3d transition metal (TM) atoms with open 3d atomic orbitals have spin and orbital polarization potentials by virtue of their 3d orbital directions, where they can play a prime important role as a spin injector or detector in spintronic fabrications by adding on non-magnetic organic materials [6]. Among these materials, interactions between transition metal (TM) atoms and bowl shaped polycyclic aromatic hydrocarbons (PAHs) are the central interest in metallo-organic chemistry, due to curved surfaces of most PAH's [7–11]. Corannulene ($C_{20}H_{10}$) was first prepared in 1966 by Barth and Lawton [12]. This molecule, with a bowl-shaped surface is one of the simplest example of curved aromatic systems which is like a fragment of C_{60} fullerene. Therefore there are two surfaces with concave and convex curvature for adsorption process. So it seems that single 3d-TM added on corannulene can be a proper candidate to design a single molecule magnet. The first π-metal adduct of corannulene was isolated by Siegel and co-workers when they isolated and spectroscopically specified corannulene [13]. There are also different sites to add TM atoms on this molecule ($\eta^2;\eta^4;\eta^5$ and η^6). Moreover, a study by Kandalam and co-workers shows that in the neutral Fe-corannulene complex, the hollow site of six-membered ring (η^6) is the most favoured binding site for the Fe atom but there is a small energy difference between convex-(η^6) and concave-(η^6) binding sites. The hollow binding site of the pentagon ring (η^5) could not be formed in neutral Fe-corannulene [14]. In addition, Dunbar has worked on binding of TM ions and alkali-ions on corannulene's surfaces [15] and found different binding sites. he has investigated Ti^+, Cr^+ and Ni^+ between open 3d shell transition metal atoms and has found η^6 of convex surface as the most favorable site for Ti^+ and Ni^+ while for Cr^+ on convex surface the η^5 site is reported equally good. To the best of our knowledge there is no systematic study on the magnetic properties of individual atoms of TM-corannulene especially no previous study on orbital magnetism of TM-corannulene complexes. On the other hand since corannulene is also known as an organic semiconductor, adding 3d transition metal atoms on its surfaces would be a potential candidate for magnetic diluted semiconductor. Therefore in the present work, adsorption of 3d transition metal atoms on both concave and convex surfaces and determination of magnetic properties of these complexes in the presence of spin–orbit coupling as a direct relativistic effect are of our interest.

The paper is organized as follow: Section 2 contains details about numerical approach. Section 3 presents the results and discussions (calculated magnetic and orbital moments, binding energies, HOMO–LUMO gap energies, etc.). Finally the paper is summarized in Section 4.

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http://dx.doi.org/10.1016/j.commatsci.2015.10.018
0927-0256/

2. Computational method

All calculations were performed using relativistic density functional theory [16] implemented within a self-consistent full-potential local-orbital basis band structure method FPLO-9 package [17]. In this scheme, scalar relativistic (SR) approach were used within a spherical average on spin–orbit interaction. The full relativistic density functional theory calculations have also been implemented self-consistently on the four-component Kohn–Sham–Dirac (KSD) equation, which implicitly contains spin–orbit coupling up to all orders. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof were used for exchange and correlation functional [18]. To get an upper estimate of orbital magnetism we used an orbital polarization (OP) correction to the GGA functional suggested by Eriksson et al. [19] and extended by Eschrig et al. [20,21] in a spin dependent form for incompletely filled d-shells. The following basus set was adopted as the valence states including (3s,3p,3d,4s,4p,4d,5s), (1s,2s,2p,3s,3p,3d), and (1s,2s,2p) for 3d transition metals, carbon, and hydrogen atoms, respectively. We have added a single 3d transition metal on the most symmetric site of corannulene, the hollow site of pentagon ring (η_5) with initial height of 1.5 Å for both concave and convex surfaces (see Fig. 1). In order to optimize atomic geometries, the position of all carbon and hydrogen atoms were fully relaxed. The force convergence accuracy was less than 0.001 eV/Å with energy convergence of 0.001 meV. The formation energy for corannulene is determined to be −157.62 eV according to

$$E_f = E_t - E_a, \tag{1}$$

where E_t is the total energy for the relaxed configuration of corannulene, E_a is sum of the total energies of all single atoms and E_f is the formation energy.

3. Results and discussion

As a starting point of discussion, our relaxation calculations show that η^5 site is the most stable position for adsorption of 3d TM atoms on concave surface with the exception of Sc which is located on the top of C–C bond of pentagon ring (η^2 site). For convex surface the most stable site is η^6, with the exception of Fe, Co and Ni which are stable on η^5 site. Relaxed positions of 3d TM atoms on both corannulene surfaces are given in Table 1.

The energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of TM-corannulene complexes are also calculated ($\triangle_{H-L}$ values in the Table 1). One can conclude that the HOMO–LUMO gaps of these complexes are significantly decreased in the presence of 3d TM atom compared to the HOMO–LUMO gap of pure molecule (3.0 eV). The electron occupation numbers of the HOMO levels (n_h) are also given in Table 1. The contribution of 3d orbitals of TM atoms (α values) and 2p orbitals of all carbons (β values) into the HOMO levels are also reported in Table 1. It can be seen that the HOMO levels in both concave and convex curvatures were formed mostly with 3d orbitals of TM atoms with the exception of Sc for concave surface and Ti for convex surface in which 2p orbitals of carbon atoms have significant contribution to their HOMO levels.

Binding energies E_b were also calculated according to

$$E_b = E_{tot} - E_{TM} - E_M, \tag{2}$$

where E_{tot} is total energy of the complex, E_M is the total energy of the pure molecule and E_{TM} is the total energy of the TM atom in its free state. All energies were calculated in magnetic regime. The calculated binding energies in scalar and full relativistic regimes are given in Table 2 and variation of binding energies in the full relativistic scheme were compared in Fig. 2. Our full relativistic calculations show that the binding energies of TM atoms added on

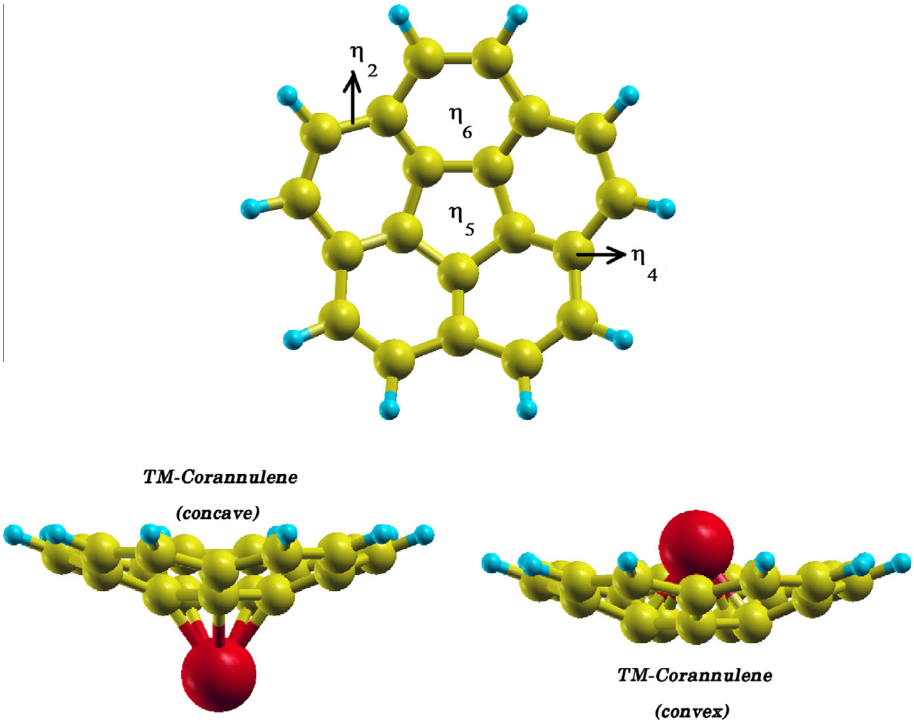

Fig. 1. (Top-panel) Corannulene molecule: yellow (blue) spheres are carbon (hydrogen) atoms with different adsorption sites. (Bottom panel) 3d transition metal atom (red spheres) added on concave and convex surfaces of corannulene. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)