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Density functional study on the adsorption and dissociation of nitroamine over the nanosized tube of MgO

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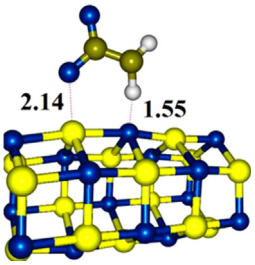
HIGHLIGHTS

- The adsorption of nitroamine molecule was investigated on an MgO nanotube (MgONT).
- Dissociation of nitroamine at the open ends of MgONT is thermodynamically feasible.
- Electronic properties of MgONTs were slightly changed after the adsorption process.

GRAPHICAL ABSTRACT

The adsorption of nitroamine molecule was investigated on an MgO nanotube using density functional theory.



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ABSTRACT

The adsorption of nitroamine (NH_2NO_2) molecule was investigated on an MgO nanotube (MgONT) using density functional theory in terms of energetic, electronic and geometric properties. It was found that adsorption and dissociation energies of NH_2NO_2 on the tube are about 20.7–47.7 and 24.9–49.6 kcal/mol, respectively. We found that the dissociation of nitroamine at the open ends of MgONT is thermodynamically feasible. Density of states analysis shows that the electronic properties of the MgONT were slightly changed after the adsorption and dissociation of NH_2NO_2 molecule.

1. Introduction

Since the last two decades, carbon nanotubes (CNTs) [1] have attracted many research scholars from all over the world because of their exciting mechanical, electronic, magnetic, and thermodynamic properties in the various fields of nanoelectronic devices, energy storage, chemical probes, biosensors, field emission displays and medical monitoring [2,3]. Because of high surface to volume ratio, CNTs are suitable for the adsorption of atmospheric gas molecules. The change in electronic and structural properties of CNTs and their exposure to environmental gases have been studied by experimental and theoretical methods [4,5]. Nanotube structures are not limited to carbon; numerous inorganic nanotubes have been prepared as well [6–10].

Recently, magnesium oxide nanotubes (MgONTs) have attracted considerable interest because of the development of their synthesis methods and the study of their remarkable properties [11,12]. Solid MgO is known as an inert material with a high melting point, consistent with strong ionic bonding, as a typical wideband gap insulator. Pure MgONTs are attractive as important metal-oxide

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quasi-one-dimensional nanostructures for applications in catalysis, as an additive in refractory and superconductor products [13]. Previous theoretical simulations [14,15] of MgONTs have shown that the morphology of MgONTs turns out to be very sensitive to their size and to the number of atomic layers forming the tube walls. For example, single-walled tubes adopt a cylindrical shape, whereas triple-walled MgO tubes retain the shape of square prisms with smoothed edges (as MgONTs synthesized) and their bond lengths and thermal stability are close to the corresponding values of crystalline magnesium oxide [15].

Understanding and controlling the physical and chemical mechanisms behind reactions in heterogeneous catalysis stand as one of the long-term goals for surface science, and also, a sound understanding of the chemical reaction is a fundamental aim of chemistry. The MgO has been considered as an ideal system in order to study the catalytic properties of oxides, particularly because of its very simple cubic crystalline structure. It comes mainly from the strong Lewis basicity of surface oxygen anions. It is believed that several reactions of catalytic interest comprise primarily the rupture of a heterolytic bond where the basic character of an O^{2-} anion predominates over the acid character of an Mg^{2+} cation. This behavior can be observed in relatively simple reactions such as the H_2 dissociation [16].

Nitroamine (NH_2NO_2) is the simplest prototype of nitramine energetic materials. In particular, the reaction of NH_2NO_2 with metal oxide surfaces is a catalytically important reaction [17]. By studying this reaction one can enhance the designing of NH_2NO_2-based catalysis, and provide fundamental insights into the bond making/breaking involved, which will contribute to a better understanding of the properties of nitro-containing compounds of energetic materials on metal oxide surfaces. To clarify some of the fundamental issues related to the interaction of energetic materials, especially nitro compounds with the MgO surface, our work focuses on the atomic-level description of the interaction between the energetic compound of nitroamine and the MgO surface. In the current study, the interaction of NH_2NO_2 with an MgONT will be investigated through density functional theory (DFT) based on analyses of structure, energies, electronic properties, stability, etc.

2. Computational methods

Geometry optimizations, energy calculations, density of states (DOS), frontier molecular orbitals (FMO), natural bond orbitals (NBO) and molecular electrostatic potential (MEP) analyses were performed on an MgONT and different NH_2NO_2/MgONT complexes. The B3LYP functional augmented with an empirical dispersion term (B3LYP-D) with 6–31G (d) basis set was used as implemented in GAMESS suite of program [18]. The B3LYP, which is a combination of HF with a DFT based on the Becke three-parameter exchange coupled with the Lee–Yang–Parr (LYP) correlation potential [19], is one of the most popular hybrid density functional methods used in nanostructure studies [20–22]. GaussSum program has been used to obtain the DOS results [23]. With the optimized structures, the adsorption energy (E_{ad}) of the NH_2NO_2 on the pure nanotube is obtained using the following equation:

$$E_{ad} = E(NH_2NO_2) + E(MgONT) - E(NH_2NO_2/MgONT) \quad (1)$$

where E (NH_2NO_2/MgONT) is the total energy of the NH_2NO_2 adsorbed form of MgONT and E (NH_2NO_2) is referred to the energy of an isolated NH_2NO_2. E (MgONT) is the energy of MgONT. The positive value of E_{ad} indicates the exothermic character of the adsorption. To investigate the electronic charge changes through the MgONT, the net charge-transfer (Q_T) between NH_2NO_2 molecule and the tube is calculated by using NBO analysis, which is defined as the charge difference between the NH_2NO_2 molecule adsorbed on the MgONT and an isolated NH_2NO_2 molecule.

3. Results and discussion

We first optimized the structures of (6,5) MgONT as a model. As shown in Fig. 1, in the nomination of the tube, number 6 is referred to the number of atoms locating at the open end of the tube (as a six-membered ring) and number 5 is referred to the number of atom layers in the nomination of the tube. The calculated Mg–O bond length of the MgONT was found to be about 1.95 Å and the average diameter was about 3.95 Å. We obtained a rippled surface similar to that of single-walled boron nitride nanotubes [24]: the more the electronegative atoms (O atoms) move outward, the more the electronegative atoms (Mg atoms) move inward. It should be mentioned that a small deviation from planarity of the initial polygons is observed. Wilson has obtained similar but slightly more distorted structures using an empirical compressible ion potential model [25]. There are two types of atoms in MgONT; terminal atoms (Mg_T and O_T) are at the open ends of tube, while central atoms (Mg_C and O_C) are in center of the tube. Two types of Mg–O bonds can be found: one of them in parallel with the tube axis, and another not in parallel with the tube axis (diagonal).

3.1. Adsorption of NH_2NO_2 on MgONT

There are two kinds of N atoms in the molecule: one is attached to two H atoms (N1, amino group) and another bonded to two oxygen atoms (N2, nitro group). In order to obtain stable configurations (local minima) of single NH_2NO_2 adsorbed on the tube, various possible initial adsorption geometries including single (hydrogen, N1, N2 or oxygen), double (H–N1, O–N2 or N1–N2) and triple (H–N1–N2 or O–N2–N1) bonded atoms close to central and terminal atoms are considered. For the sake of simplicity, we have considered three most stable configurations (Fig. 2) in which the NH_2NO_2 molecule is as near as possible to the MgONT

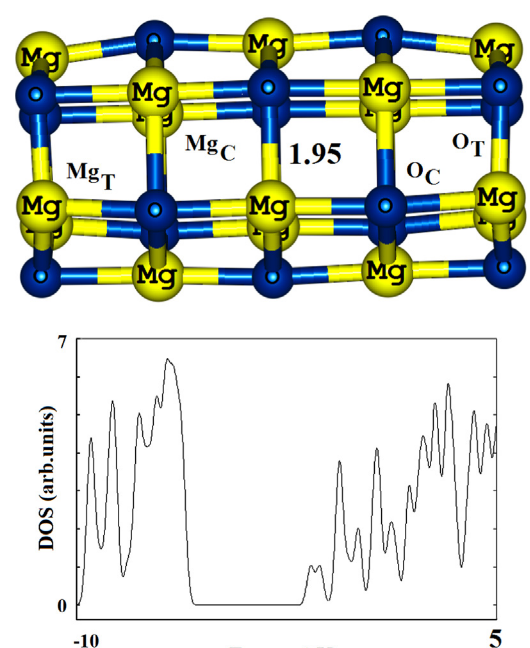

Fig. 1. (a) Geometrical parameters of the optimized MgONT and its density of states (DOS) plot. Bonds are in angstrom.