

The Alkali Metal Interactions with MgO Nanotubes

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Adsorption of alkali metals (Li, Na, and K) on the surface of magnesium oxide nanotubes (MgONTs) with different diameters was investigated using density functional theory. According to the obtained results, the most stable adsorption site was found to be atop the oxygen atom of the tube surface with adsorption energies in the range of -0.25 to -0.74 eV. HOMO-LUMO gap (E_g) of the tubes dramatically decreases upon the adsorption of the alkali metals, resulting in enhancement of their electrical conductivity enhancement. The order of E_g decrement caused by the metal adsorption is as follows: $K > Na > Li$. The results suggest that the MgONTs were transformed from semi-insulator to semiconductor upon the alkali metal adsorption. Increasing the tube diameter, the HOMO/LUMO gap of the pristine tube is enhanced and adsorption energies of the alkali metals are decreased.

Key Words : Alkali metal atom, Magnesium oxide nanotubes, Density functional theory, Adsorption, M05

Introduction

Metal nanoparticles have been extensively studied due to their promising various applications such as catalysis, chemical sensing, and fabrication of micro-electric and magnetic devices.¹⁻³ Metal oxides are the most important and widely studied nanostructures that have been significantly utilized in different areas including chemical/biological sensors, lasers, and displays.⁴ Alkali and alkaline earth metals are known to act as reaction modifiers on a variety of substrates including metal oxides. However, a few studies have been carried out about the alkali and alkaline earth metal adsorption on the MgO sheets so far.⁵ Interaction of lithium with MgO surface is one of the classical examples which transform the MgO into a catalyst capable of methane activation presumably by the creation of electron deficient oxygen centers.⁶

Recently, Finazzi *et al.* have systematically investigated the properties of small amounts of alkali metal atoms (Li, Na, and K) deposited on different sites of MgO surfaces by means of electron paramagnetic resonance (EPR) spectroscopy and density functional theory (DFT).⁷ They showed that all of the atoms bind preferentially to the surface oxide anions, but the location of these anions differs as a function of the deposition temperature and the alkali metal. Inter-calation and encapsulation of the alkali metals in carbon nanotubes (CNTs) affect the electronic and structural properties of the tubes⁸ and show a significant reduction of the work function⁹, resulting to the improvement of the emission properties. Soon after the discovery of CNTs, one of their isoelectronic structures, magnesium oxide nanotubes (MgONTs) were predicted by theoretical calculations^{10,11} and then experimentally synthesized.¹² MgONTs have re-

cently attracted great interest due to the development of their synthesis methods and their remarkable properties. Pure MgONTs, as important metal-oxide quasi-one-dimensional nanostructures, are attractive for various applications in catalysis, as an additive in refractory and superconductor products.¹³ Very recently, we have shown that the MgONTs can selectively detect NO molecules in the presence of gaseous CO.¹⁴

Herein, we have reported a theoretical study about the adsorption of alkali metals of Li, Na, and K on the surface of MgONTs with different diameters through DFT calculations. The interaction of the alkali metals with the oxide materials is relevant to a wide number of problems and applications and usually changes the electrical and conductivity of the materials. In some cases such as tungsten bronzes this may lead to an insulator-metal transition. It is noteworthy that the addition of alkali metals to the layered materials is essential for the preparation of ionic conductors and new generations of batteries.

Computational Methods

Geometry optimizations were performed on different MgONTs including 4×5 , 6×5 , and 8×5 types and their alkali metal-adsorbed complexes at the spin-unrestricted M05/6-31G* level of theory. All of the energy calculations, charge and density of state (DOS) analyses were done using 6-311+G* basis sets with the same functional. In terms of nomenclature, the first number is referred to the numbers of atoms locating at the open end of the tubes and the latter is referred to the numbers of atom layers (Fig. 1). Truhlar *et al.*¹⁵ have previously recommended the M05 functional for general purpose applications in noncovalent interactions

involving both metallic and nonmetallic elements. They have shown that this unique functional, with broad applicability to chemistry, performs very well not only for main-group thermochemistry and radical reaction barrier heights but also for metal-metal interactions. Furthermore, this functional have been previously used by other research groups to study the nanotube systems.^{16,17} We have defined the adsorption energy (E_{ad}) of the alkali metals as follows:

$$E_{ad} = E(\text{metal/MgONT}) - E(\text{MgONT}) - E(\text{metal})$$

where $E(\text{metal/MgONT})$ is the total energy of an alkali metal atom (Li, Na, or K) adsorbed on the pristine MgONT surface, and $E(\text{MgONT})$ and $E(\text{metal})$ are the total energies of the pristine MgONT and the metal, respectively. By the definition, negative values of E_{ad} correspond to the exothermic adsorptions. All calculations reported here were carried out using a locally modified version of the GAMESS electronic structure program.¹⁸

Results and Discussion

Alkali Metal Adsorption on the 6×5 MgONT. At first, we optimized the structure of the pure 6×5 MgONT as a model. The calculated Mg-O bond length of the tube surface (Fig. 1(a)) was found to be about 1.99 Å and the average diameter was 3.82 Å. A rippled surface was obtained for the optimized structure; the more electronegative atoms (O atoms) have moved outward, while the more electropositive ones (Mg atoms) moved inward. Then, three alkali metal atoms including Li, Na, and K have been considered to be adsorbed on the outside surface of the MgONTs. For each

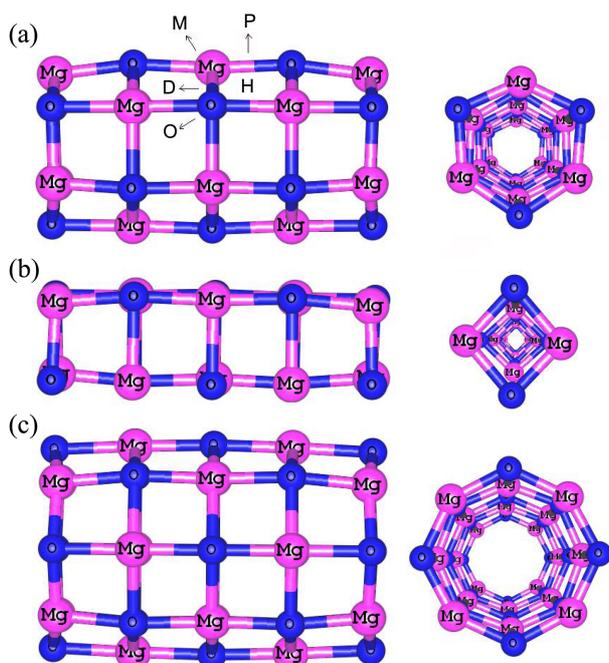


Figure 1. Optimized structure of (a) 6×5 MgONT, (b) 4×5 MgONT, (c) 8×5 MgONT and (d) Detailed description of different binding sites of a single alkali metal adsorbed on a MgONT. Mg, magnesium; O, oxygen.

Table 1. Calculated structural parameters and adsorption energies of alkali metals adsorbed on the MgONT

Tube	Metal	^a E_{ad}	^b Q	^c E_g	^d ΔE_g
4×5	Li	-0.74	0.78	1.02	3.36 (76.7%)
	Na	-0.39	0.80	0.93	3.45 (78.8%)
	K	-0.36	0.83	0.54	3.84 (87.7%)
6×5	Li	-0.70	0.69	1.17	3.31 (66.7%)
	Na	-0.38	0.70	1.05	3.43 (69.2%)
	K	-0.32	0.70	0.65	3.80 (76.6%)
8×5	Li	-0.64	0.49	1.19	3.87 (75.9%)
	Na	-0.31	0.50	1.02	4.04 (79.8%)
	K	-0.25	0.53	0.62	4.44 (87.7%)

^aAdsorption energy (eV) per atom. ^bQ is defined as the total Mulliken charge on the atoms adsorbed on the MgONT. ^cHOMO-LUMO gap (eV) of the tube after metal adsorption. The E_g of bare 4×5 , 6×5 and 8×5 nanotubes is 4.38, 4.96, 5.06 eV. ^dThe change of E_g (eV) upon the metal adsorption.

adsorbate, five different sites of adsorption (*M*, *O*, *H*, *P*, and *D*), as shown in Figure 1(a), were considered to examine the interaction between the MgONT and a single atom. To ensure that the most stable adsorption configuration achieved, the initial distance between the molecule and the tube was adjusted several times from 1.0 to 3.0 Å. Full structural relaxation was then performed with each of the initial atom-cluster distances.

After careful structural optimizations, it was found that the most stable adsorbed configuration is the one in which the metal was bonded to the Mg atom of the tube surface. This finding is generally in good agreement with the previous results of Xu *et al.*, in which they have investigated the alkali metal adsorptions on a MgO (0 0 1) surface.¹⁹ Based on our first-principle calculations, all of the metal atoms were exothermically adsorbed on the outside surface of the MgONT with negative E_{ad} . However, the E_{ad} values are rather different for the three alkali metals, whereas lithium is strongly bonded (0.70 eV), while sodium and potassium atoms form bonds with medium strength (Table 1). The metal-tube distances for the adsorbed Li, Na, and K atoms are about 1.81, 2.31, and 2.70 Å, respectively (Table 1).

As it can be seen in Figure 2, the alkali metal adsorptions induce a local structural deformation to the MgONT; the bond length of Mg-O of the tube surface is significantly increased from 1.99 Å in the free MgONT to 2.07 Å in the Li-adsorbed form, indicating their strong interaction. The longitudinal and latitudinal O-Mg-O angles are also changed from 177.01° and 116.07° to 166.28° and 107.33°, respectively. Further indication of the degree of deformation after the adsorption process is given by the bond reorganization energy (E_{br}), calculated as the energy difference between the geometry of the tube after adsorption and the full relaxed one. The calculated E_{br} is in the range of 0.21-0.77 eV, confirming high strength of the interaction.

Preferable adsorption of the alkali metals on the oxygen atom of the tube surface rather than the Mg site can be attributed to their metal characteristic and therefore having the tendency of losing their valence electron to the electro-

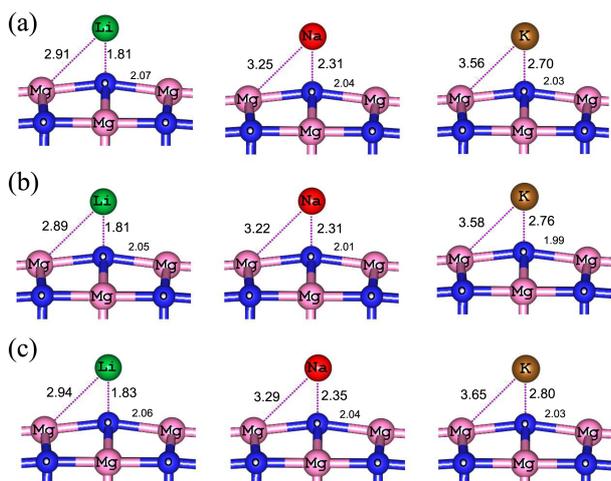


Figure 2. Optimized structure of each alkali metal atom adsorbed on (a) 6×5 MgONT, (b) 4×5 MgONT and (c) 8×5 MgONT.

negative nonmetallic oxygen. However, in the bare tube some charges are transferred from the Mg atoms to the O atoms; when an alkali metal is placed in the vicinity of an O atom of the tube surface it competes with the Mg atoms for giving the electron to the O atom. According to the obtained results, with increasing the atomic number of the alkali metals, the E_{ad} values decrease. This observation may be explained based on the Pearson's hard-soft acid-base theory (HSAB), states that the soft acids react strongly with the soft bases and in contrary, the hard acids react strongly with the hard bases, when all other factors being equal. The Li atom is a hard acid with smaller size, and is weakly polarizable compared to the other alkali metals. Therefore, it tends to interact more preferably with oxygen which is known as a hard acid, in comparison with the Na and K atoms.

In order to consider the influence of metal adsorptions on the electronic properties of the tube, we have drawn the DOS plots for both the bare and metal adsorbed tube(s) shown in Figure 3. From the DOS plot of the bare MgONT in this figure, it can be concluded that it is a semi-insulator material

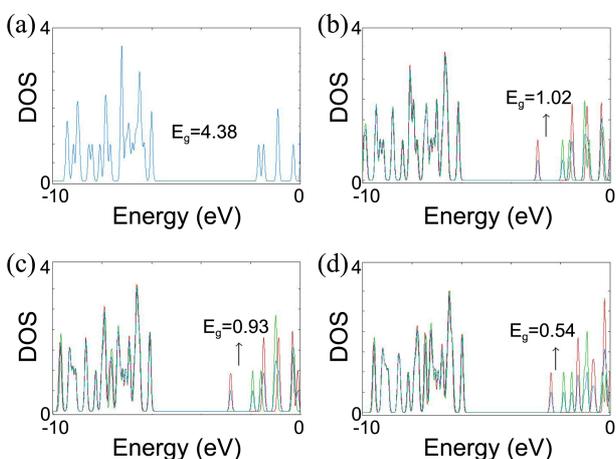


Figure 3. Comparison between the density of states for (a) the isolated 6×5 MgONT (b) Li adsorbed, (c) Na adsorbed and (d) K adsorbed on the MgONT.

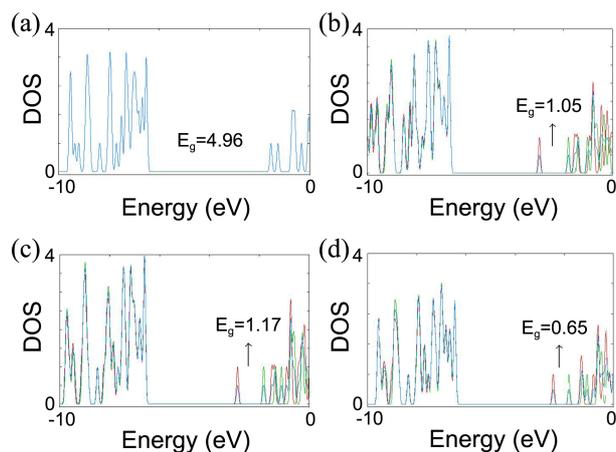


Figure 4. Comparison between the density of states for (a) the isolated 4×5 MgONT (b) Li adsorbed, (c) Na adsorbed and (d) K adsorbed on the MgONT.

with a wide HOMO-LUMO gap (E_g) of 4.96 eV. As shown in panels (b), (c), and (d) of Figure 3, the DOSs for all of the adsorbed metal configurations have a distinct change near the conduction level compared to that of the pristine tube, so that a local energy level appears after the adsorption of the metals.

Therefore, upon the metal adsorptions, E_g of the tube dramatically decreases in the all adsorption cases which would result in an electrical conductivity change of the nanotube according to the equation

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right),$$

where σ is the electric conductivity, and k is the Boltzmann's constant.²⁰ According to the equation, smaller values of E_g at a given temperature lead to larger electric conductivity. The largest decrement of E_g belongs to the case of the adsorption of K atom, in which the E_g reduces from 4.96 to 0.65 eV so that the tube is transformed from semi-insulator to a semiconductor compound. More inspection of the DOS plots (Fig. 4) reveals that in all of the cases the LUMO levels are nearly constant and the HOMO levels shift toward higher energies due to the charge transfer from the alkali metals to the tubes.

We have also put the alkali metal atoms inside of the tube to explore the interior adsorption process. To this aim, every metal atom was exactly located in the center of the tube inside, then a relax optimization was performed. Among all of the atoms, the K atom led to the tube structure decomposition and no global minima was obtained because of the convergence failure. For other two atoms positive E_{ad} values of 0.08 eV (Li) and 1.95 eV (Na) were obtained. However, the inside adsorption is not thermodynamically a favorable process.

Effect of the Tube Diameter on the Alkali Metal Adsorption. In order to explore the effect of the tube curvature, the adsorption of alkali metals on the surface of two kinds of nanotubes with smaller and larger diameters including 4×5

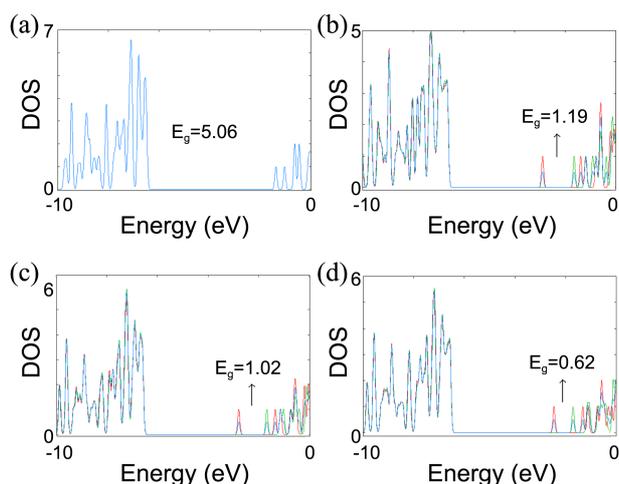


Figure 5. Comparison between the density of states for (a) the isolated 8×5 MgONT (b) Li adsorbed, (c) Na adsorbed and (d) K adsorbed on the MgONT.

and 8×5 were investigated. The optimized structures of these tubes are shown in Figure 1 and the geometry parameters of the alkali-metal/MgONT complexes are depicted in Figure 2. The results show that increasing the tube diameter results in increased E_g values. Interestingly, this trend is in contrast to that for semiconducting CNTs. It has already been showed that the band gap of the semiconducting CNTs inversely depends on the nanotube diameter.^{21,22}

It is also well known that the change of E_g influences the nanotube chemical reactivity so that a smaller E_g typically leads to a higher reactivity. As shown in Table 1, the E_{ad} is increased by decreasing the tube diameter. This might be due to the fact that upon the adsorption process, the adsorbing oxygen atom has to project out; while the thermodynamic driving force of this phenomenon is lower in the case of smaller diameter tubes because of the larger surface curvature. However in all the studied tubes, decrement of the atomic number of the alkali metals results in more negative values for E_{ad} . The plots of DOS for the 4×5 and 8×5 nanotubes and their complexes with metals are shown in Figures 4 and 5. Similar to the case of 6×5 nanotubes, the E_g of these nanotubes is dramatically increased upon the alkali metal adsorption. The results do not show a straightforward relation between the diameter of the studied tube and the change of the E_g upon the adsorption process. The changes of E_g in the cases of 8×5 and 4×5 nanotubes are larger than that in the 6×5 one.

Conclusion

We have performed a theoretical study on the adsorption

of alkali metal atoms (Li, Na, and K) on the surface of different MgONTs. All the metals prefer to bind the O atom of the tube surface rather than Mg one. Increasing the atomic number of the alkali metals, the adsorption energy decreases. Upon the metal adsorptions, the E_g of the tubes considerably decreases in all of the adsorption cases which would result in an electrical conductivity increment of the nanotubes. A semi-insulator to semiconductor transition was seen for MgONTs upon the alkali metal adsorption. By increasing the tube diameter, the HOMO/LUMO gap of the pristine tube is increased and the adsorption energies of the alkali metals are decreased.

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