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Decomposition of methanol on nanosized tube of magnesium oxide: A theoretical study

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ABSTRACT

The interaction of a methanol molecule with an MgO nanotube was investigated by using density functional calculations. It was mainly found that (1) the adsorption process is associative in the exterior surface and dissociative at the ends of the tube; (2) in the most stable states, calculated adsorption energies are about −29.5 and −35.6 kcal/mol for associative and dissociative adsorptions, respectively; (3) a small barrier energy of 5.6 kcal/mol must be overcome to get the final structure in dissociative process; (4) cleavage of O–H bond of methanol is more favorable than C–O bond cleavage about 7.0 and 8.5 kcal/mol, thermodynamically and kinetically, respectively; (5) the dissociative processes influence the electronic properties of MgO nanotube more than associative processes; and (6) HOMO/LUMO gap of the tube is significantly reduced from 4.63 to 3.94 eV upon the O–H cleavage.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) [1], quasi-one-dimensional tubular nanostructures have attracted considerable interest due to their excellent electronic properties and promising applications in building nanodevices [2–6]. CNTs can be metallic or semiconducting owing to different helicities and diameters of rolling a graphitic sheet [7]. Nanotube structures are not limited to carbon; numerous inorganic nanotubes have been prepared. Magnesium oxide $(MgO)_n$ nanostructures such as nanorods and nanotubes have been successfully fabricated and their physical properties have been investigated [8]. For $(MgO)_{12}$, previous theoretical studies indicated that the tube-like ground state is more stable than cage and cubic isomers [9,10]. In experiment, observations from mass spectra [11] revealed that small MgO clusters prefer the nanotube geometry to the bulk-like structure.

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 in chemistry. The MgO has been considered as an ideal system in order to study the catalytic properties of oxides, fundamentally due to 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 H_2 dissociation [12]. In particular, the reaction of methanol (CH_3OH) on metal oxide surfaces is a catalytically important reaction. By studying this reaction, one can enhance the understanding of CH_3OH based catalysis, and provide insights into the fundamentals of bond making/breaking involved, which will contribute to a better understanding of carbon monoxide hydrogenation and CH_3OH synthesis. Furthermore, the decomposition reaction of CH_3OH itself is currently attracting widespread attention due to its possible usage as a hydrogen source in fuel cell applications [13]. In the adsorption of CH_3OH, two bonds, specifically O–H and C–O, can play a role in the dissociation and transformation of this molecule. Theoretical and experimental results [14,15] have indicated that the most stable and stoichiometric (001) face of MgO is inert for dissociation of methanol. The adsorbed molecule is linked by a hydrogen bond with the surface where the hydroxyl of CH_3OH and an O^{2-} anion of the surface participate. In the current work, the interaction of CH_3OH with an MgONT will be investigated using density functional theory (DFT) based on analyses of structure, energies, electronic properties, stability, etc.

2. Computational methods

Spin-unrestricted B3LYP hybrid DFT method within 6-31G (d) all electron basis set was used for the optimization, density of states (DOS), frontier molecular orbitals (FMO), molecular electrostatic potential (MEP) analyses and energy calculations. The B3LYP has been demonstrated to be a reliable and commonly used level of

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theory in the study of different nanostructures [16–20]. With the optimized structures, the adsorption energy (E_{ad}) of the CH_3OH on the pure nanotube is obtained using the following equation:

$$E_{ad} = E(CH_3OH/MgONT) - E(MgONT) - E(CH_3OH) \quad (1)$$

where $E(CH_3OH/MgONT)$ is the total energy of the CH_3OH adsorbed form of MgONT and $E(CH_3OH)$ is referred to the energy of an isolated CH_3OH. The $E(MgONT)$ is the energy of MgONT. The negative value of E_{ad} indicates the exothermic nature of the adsorption. All calculations were carried out using GAMESS electronic structure program [21]. To investigate the electronic charge changes through the MgONT, the net charge transfer (Q_T) between CH_3OH molecule and the tube is calculated by using Mulliken population analysis, which is defined as the charge difference between the CH_3OH molecule adsorbed on the MgONT and an isolated CH_3OH molecule.

3. Results and discussion

The MgONT can be assumed as the tube resulting from a rolled tetragonal sheet of MgO. Here, we selected a 6×5 tube in which the first number is referred to the number of atoms locating at the open end of the tubes and the latter is referred to the number of atom layers. Fig. 1a presents optimized structure of the MgONT which is used with rippled surface similar to that of previously reported for single-walled boron nitride nanotubes [22]. 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 [23]. There are two types of atoms in MgONT; terminal atoms (Mg_T and O_T) are in the open end of the tube, while central atoms (Mg_C and O_C) are in the 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). In order to obtain the stable configurations of a single adsorbed-CH_3OH on the tube, various possible initial adsorption geometries on different adsorption sites were considered. The results indicate that the CH_3OH can be adsorbed on the surface of the tube or chemically dissociated into different fragments on an Mg–O bond of the tube surface.

3.1. Associative adsorption of CH_3OH on MgONT

There are several individual sites for the adsorption of a CH_3OH; on the top of either Mg or O atom. Therefore, to find the adsorption behavior of a CH_3OH molecule on the tube, the O and H atoms of molecule was located atop of central and terminal atoms, separately. For the sake of simplicity, we have considered three most stable configurations (Fig. 2) in which the CH_3OH molecule is as near as possible to MgONT including: (**A.1**) the CH_3OH molecule is bonded via oxygen atom to a Mg_C atom, also an H-bonding is formed between O_C and hydrogen atom of hydroxyl group, (**A.2**) the CH_3OH molecule is bonded via oxygen atom to a Mg_T atom, also an H-bonding is formed between O_T and hydrogen atom of methyl group and (**A.3**) the CH_3OH molecule is bonded via oxygen atom to a Mg_T atom, also an H-bonding is formed between O_T and hydrogen atom of hydroxyl group. More detailed information including values of E_{ad} and the charge transfer (Q_T) is listed in Table 1.

Notice that the adsorption is site selective, so in all cases the hydroxyl group is reoriented in such a way that the O atom of methanol is directly linked to an Mg cation while the methanol H atom is directly linked with an O anion. The adsorption of the O atom of CH_3OH preferably on the Mg atom of the tube surface, rather than on the O site, can be attributed to low ionization potential of Mg and, therefore, having the tendency of losing their valence electron to the electro-negative oxygen. However, in the bare tube, some charges are transferred from the Mg atoms to the O atoms; when an O atom is placed in the vicinity of an Mg atom of the tube surface, it competes with the O atoms of surface for receiving the electron from the Mg atom. Based on Mulliken population analysis, the point charge of magnesium and oxygen in MgONT is +0.910 *e* and −0.910 *e*, respectively, which is in agreement with our calculated MEP. As shown by the mapped-MEP of MgONT in Fig. 1b, the Mg atoms are positively charged (blue colors), while the O atoms are negatively charged (red colors) in Mg–O bonding. Thus, it seems that Mg atoms are suitable sites for nucleophilic attack of CH_3OH.

As shown in Table 1, the E_{ad} values corresponding to various adsorption configurations are in the range of −22.2 to −29.5 kcal/mol. The configuration **A.3** gives rise to an E_{ad} of −29.5 kcal/mol, which is more negative than the E_{ad} values for **A.1** (−22.2 kcal/mol) and **A.2** (−26.0 kcal/mol) configurations. Corresponding newly formed O–Mg bond between the molecule and the tube in these configurations are ranged from 2.06 to 2.11 Å

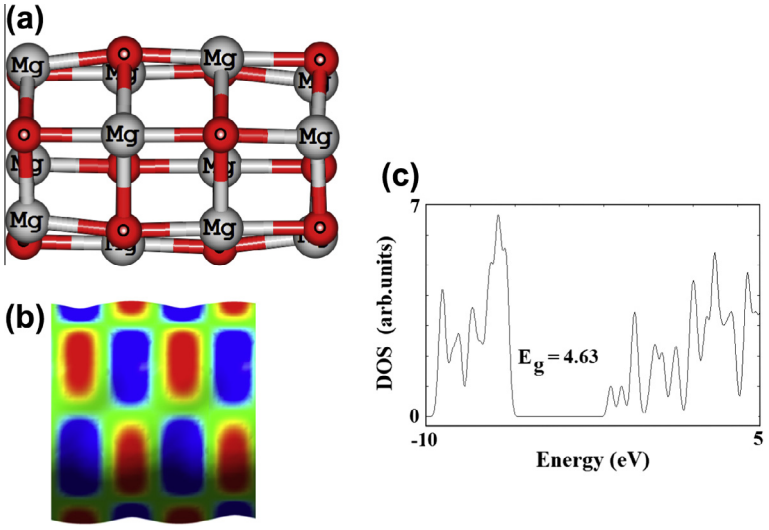

Fig. 1. (a) Geometrical parameters of the optimized MgONT. Bonds are in Å. (b) The calculated molecular electrostatic potential surface (MEP) of the MgONT. The red and blue colors are referred to the higher and lower electron densities, respectively. (c) Density of states (DOS) of MgONT. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)