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Theoretical structural study on the adsorption properties of aliphatic aldehydes on ZnO nanoclusters and graphene-like nanosheets systems

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HIGHLIGHTS

- Theoretical study of the adsorption of aldehydes on ZnO nanoparticles.
- Hydrogen-terminated ZnO nanoclusters and graphene-like nanosheets are considered.
- Densities of states of the aldehydes into ZnO surfaces are calculated.
- Effect of aldehyde chain length was investigated.

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ABSTRACT

The structure optimizations for some aliphatic aldehydes adsorbed on ZnO nanoclusters, and graphene-like nanosheets were carried out using the B3LYP/LanL2DZ calculations and the adsorption energies were calculated. It was considered that adsorption of the examined aldehydes on the ZnO nanoclusters and graphene-like nanosheets occurred through carbonyl oxygens of aldehyde molecules with the surface Zn^{2+} ions of the central ring. Aldehydes with the general formula of R–COH (R denotes a branched or linear aliphatic chain with maximum of three carbon atoms) were considered. Also, Effects of chain length were investigated on the orientation of the aldehyde molecules with respect to the nanosheet and nanocluster surfaces. Findings revealed that the adsorption energy was decreased with enhancing chain length. However, the most negative adsorption energy was obtained for iso-butyraldehyde, as a branched aldehyde. Interaction of the aldehyde molecules with the surfaces of nanosheets were analyzed by means of DOS analysis and Bader's method. We hope the obtained results be helpful in identifying the mechanism of cyclotrimerization of aliphatic aldehydes on the surface of zinc oxide nanoparticles.

1. Introduction

Bulk and nano-sized zinc oxides are unique materials which have prompted much interest in the field of catalysis in the past decades [1]. Different morphologies along with a wide range of particle sizes for ZnO have led to diverse investigations for academia and industrial purposes such as excellent performances in optics, electronics, piezoelectricity [2] and photoelectronics [3]. In the last few years, much attention has been devoted to zinc oxide and its nanostructures. ZnO is a semi-conductive metal oxide with a wide band gap which has shown high prospects in optoelectronics, especially because of its high excitation binding energy [4].

Different surfaces such as planar graphite-like [5] and wurtzite structures have been studied theoretically for ZnO [6]. Moreover, different shapes for ZnO nanostructures, such as nanorods [7], nanowires [8–10], nanocombs [11], nanorings [12] and nanotubes [13,14] have been explored and their properties are investigated. During the last decade, substantial efforts have been carried out in understanding the adsorption of small molecules on oxide surfaces according to detailed theoretical calculations [15,16]. Among the most studied examples, ZnO surfaces occupied a unique position, because of their satisfying descriptions which could be obtained [17–21]. Recently, the structure optimizations of all configurations of H_2O and NH_3 adsorbed on different surfaces of ZnO nanoclusters and nanosheets were achieved using B3LYP/LanL2DZ calculations [22]. Moreover, the single ZnO monolayer with graphene-like structure is synthesized and some of its optoelectronical properties are investigated [23].

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In the present research, adsorption of some aliphatic aldehydes on ZnO nanoclusters (ZnONCs) including aromatic-like (AL-ZnONC, $Zn_3O_3H_6$), naphthalene-like (NLL-ZnONC, $Zn_5O_5H_8$) and graphene-like nanosheets ZnOGLNSs involving coronene-like (CNL-ZnONS, $Zn_{12}O_{12}H_{12}$) and circumcoronene-like (CCL-ZnONS, $Zn_{27}O_{27}H_{18}$) are studied by using B3LYP/LanL2DZ theoretical methods [22].

Moreover, the densities of states (DOS) of the adsorbed aldehydes into different ZnO surfaces were calculated in order to analyze the adsorbate–substrate interactions. In particular, bonding interactions during molecular adsorption of ethanal, propanal, butanal, and iso-butyraldehyde onto the surfaces of ZnONCs and ZnOGLNSs, including orbital occupation analysis, were investigated [24].

2. Computational details

Geometry optimizations were performed to model the adsorption of the desired aldehydes on the aromatic-like (AL-ZnONC, $Zn_3O_3H_6$), naphthalene-like (NLL-ZnONC, $Zn_5O_5H_8$), coronene-like (CNL-ZnONS, $Zn_{12}O_{12}H_{12}$) and circumcoronene-like (CCL-ZnONS, $Zn_{27}O_{27}H_{18}$) surfaces using density functional theory (DFT) method. The calculations have been performed with hybrid density functional B3LYP, the Becke three-parameter hybrid function combined with the Lee-Yang-Parr correlation functional [25,26], using the Los Alamos LanL2DZ split-valence basis set [27,28]. All calculations were performed with the Gaussian 09 program [29]. The B3LYP/LanL2DZ-optimized structures of the AL-ZnONC, NLL-ZnONC, CNL-ZnONS, and CCL-ZnONS were obtained from the full geometry optimizations, as indicated in Fig. 1.

The adsorption energies of aldehydes adsorbed on the clean surfaces of ZnOGLNS computed by Eq. (1):

$$\Delta E_{ads} = E_{RCOH/ZnO} - (E_{RCOH} + E_{ZnO}) \quad (1)$$

Where $E_{RCOH/ZnO}$ is the total energy of aldehyde molecule adsorbed on the ZnO surfaces. E_{RCOH} and E_{ZnO} are total energies of the isolated aldehyde and the clean surface of ZnO, respectively.

The adsorption energies of aldehydes on the AL-ZnONC and CNL-ZnONS computed using the B3LYP/LanL2DZ method; however, a counterpoise correction [30] for basis set superposition error (BSSE) was also applied.

Geometry optimizations and density of states (DOS) analysis were performed on nanoclusters and nanosheets with the spin restricted B3LYP/LanL2DZ [31–33]. GaussSum program [34] has been used to obtain the DOS spectra. The B3LYP demonstrated a reliable and common functional in the study of different nanostructures [35–38]. Vibrational frequencies were also calculated at the same level to confirm that all the stationary points corresponded to the true minima on the potential energy surfaces. All frequency calculations were performed using numerical second derivatives and verified that all the structures were true minima by frequency analysis and obtained positive Hessian Eigen value [39].

An alternative approach to the analysis of atomic charges was proposed by Bader [40]. In the Bader's method, the central point serves to determine the region that relates to each atom by analyzing the topological properties of the charge density. The AIM2000 program [41] was used in order to calculate the topological properties of the $Zn\cdots O_{aldehyde}$ interactions of different systems. In the present paper, an implementation of the Bader's method is also applied [24,42].

3. Results and discussion

3.1. Study of the adsorption modes of aldehydes on the ZnO surface

The B3LYP/LanL2DZ-optimized structures of adsorption configurations of ethanal adsorbed on the full relax structures of the

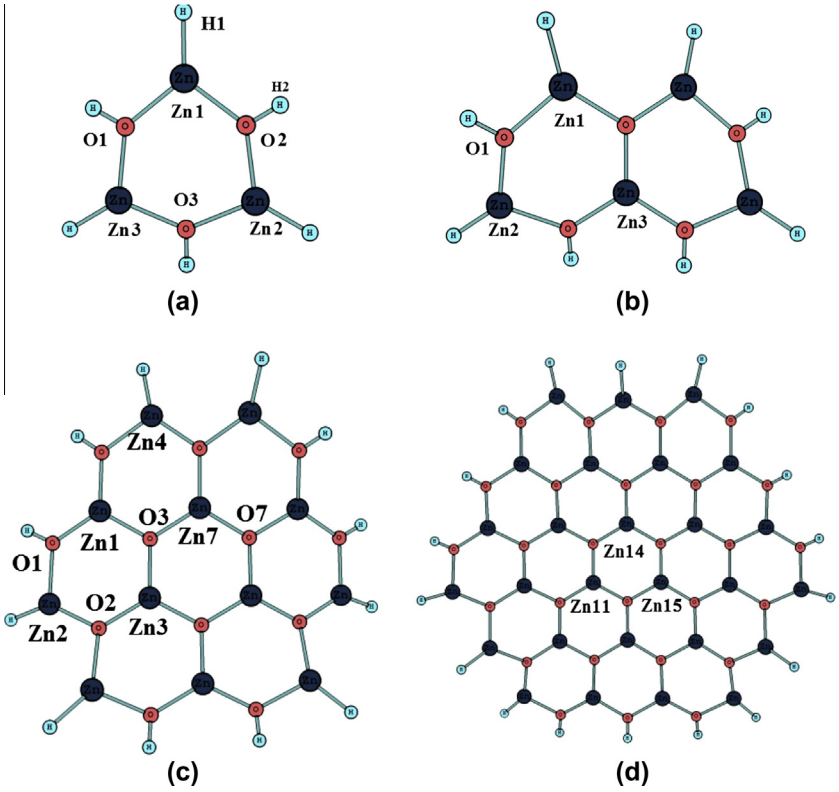

Fig. 1. The B3LYP/LanL2DZ-optimized structures of (a) the aromatic-like ZnO nanocluster (AL-ZnONC), (b) naphthalene-like ZnO nanocluster (NLL-ZnONC), (c) coronene-like ZnO nanosheet (CNL-ZnONS) and (d) circumcoronene-like ZnO nanosheet (CCL-ZnONS).