Research Article

Open Access

Tooba Afshari¹ and Mohsen Mohsennia^{1,2,*}

Transition metals doped ZnO nanocluster for ethylene oxide detection: A DFT study

<https://doi.org/10.1515/mgmc-2019-0012>

Received November 19, 2018; accepted April 24, 2019.

Abstract: Density functional theory (DFT) studies at B3LYP/6-31G (d) (Becke, 3-parameter, Lee-Yang-Parr) level were performed to evaluate adsorption interactions between ethylene oxide (EO) molecule, and pristine and transition metals (TM) (i.e., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) doped ZnO nanocluster (TM-doped Zn₁₂O₁₂). The adsorption energy (E_{ad}), band gap energy (E_g), Mulliken charge transfer (Q_t) and molecular electrostatic potential (MEP) were calculated to examine the sensitivity of the Zn₁₂O₁₂ and its TM-doped forms toward EO detection. It was found that in contrast to the pristine Zn₁₂O₁₂, the electronic properties of TM-doped Zn₁₂O₁₂ were sharply sensitive to the presence of EO gas molecules. The results revealed that among the studied TM-doped Zn₁₂O₁₂, Cr- and V-doped Zn₁₂O₁₂ have great potential applicability as EO sensor, due to their highest E_g change (ΔE_g) values, after the EO adsorption. Moreover, the density of state (DOS) calculations confirmed that strong electronic interaction between Cr- and V-doped Zn₁₂O₁₂ and EO molecules can makes them interesting empirical candidate for detection and adsorptive removal of EO gas molecules.

Keywords: ethylene oxide; DFT; transition metals; ZnO nanocluster; gas sensor

1 Introduction

Ethylene oxide (EO) is a colorless, flammable and highly reactive gas at the ambient temperature, having

a slightly sweet odor (Bashir et al., 2016). EO (C₂H₄O) is the smallest cyclic ether which has been utilized in some industrial production processes such as solvents, antifreeze, pesticide, sterilization, textiles and pharmaceuticals (Rebsdatt and Mayer, 2001). Exposure to toxic gas EO molecule may cause to dizziness, convulsions, cataracts, skin allergy, central neuropathy, and cancer (Steenland et al., 1991). Consequently, to protect human health and the environment purpose, detection of EO in the atmosphere using low cost, easy operation and sensitive gas sensors seems to be an important issue to research.

Due to their small size, low-power need, high detection sensitivity and low cost production, the recent sensitive solid state sensors are widespread devices for detection of hazardous and toxic gases in the environment (Capone et al., 2003). During the recent years, the low sensitivity of bulk materials in sensor fabrication processes has been overcome by developing exploring some new-generation of nanomaterials with the unique properties and many potential applications, ranging from electronics to chemical sensors (Afshari and Mohsennia, 2018; Beheshtian et al., 2012a; Mahdavian, 2012; Mohsennia et al., 2018; Rakhshi et al., 2018; Rezaei-Sameti and Yaghoobi, 2015; Yoon et al., 2011). Metal oxides, such as MgO, ZnO, BeO, WO₃, SnO₂, and TiO₂, are commonly employed in chemical gas sensors, changing the electrical conductivity of these materials upon adsorption of gaseous molecules (Beheshtian et al., 2012b; Beheshtian et al., 2013a; Degler et al., 2016; Epifani et al., 2016; Kakemam and Peyghan, 2013; Kerkez and Boz, 2014; Kim et al., 2015; Peyghan and Noei, 2014; Peyghan and Yourdkhani 2014; Samadizadeh et al., 2015; Yang and Yao, 2000; Ziat et al., 2014;).

The ZnO is a semi-conductive metal oxide with a wide direct band gap which has high prospects in optoelectronics, especially because of its high excitation binding energy (Duan et al., 2006). ZnO nanostructured materials including nanowires, nanotubes, nanoclusters, and nanoparticles have been frequently probed as sensors for different gases including such as F₂, NH₃, CH₄, O₂, NO and CO (Lahmer, 2016; Peyghan and Noei,

* Corresponding author: Mohsen Mohsennia, Department of Chemistry, University of Kashan, Kashan, Iran; Institute of Nanoscience and Nanotechnology, University of Kashan, Kashan, Iran, Tel.: +98 31 55913065; Fax: +98 31 55912397, e-mail: m.mohsennia@kashanu.ac.ir

Tooba Afshari, Department of Chemistry, University of Kashan, Kashan, Iran

2013; Peyghan et al., 2014; Peyghan et al., 2015). Because of low sensitivity of the substrate materials for sensing applications, different methods such as metal doping, non-metal doping and vacancy-defect have been developed to manipulate their geometry to enhance the electron transport and electronic properties (Alver et al., 2018; Aslanzadeh, 2016; Gong et al., 2006; Hadipour et al., 2015; Özgür et al., 2005; Sahay and Nath, 2008; Zhu et al., 2012). Among the various doping substances and strategies, the incorporation of few percent of transition metal (TM) ions into semiconducting oxide materials has shown the enhancement of both electronic and magnetic properties due to oxygen vacancies and created interstitial vacancies at host lattice positions (Ivanov et al., 2004; Kaushik et al., 2013; Marcel et al., 2005).

In this study, first-principles density functional theory (DFT) calculations have been performed on the electronic structure of TM-doped $\text{Zn}_{12}\text{O}_{12}$ (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) to evaluate the effect of metal dopants on the geometric structure and electronic structure of $\text{Zn}_{12}\text{O}_{12}$ to explore behavior of pristine and TM-doped $\text{Zn}_{12}\text{O}_{12}$ in the presence of EO molecules. Here, some theoretical parameters such as adsorption energy (E_{ad}), band gap energy (E_g), global hardness (η), Mulliken charge transfer (Q_{r}), molecular electrostatic potential (MEP) and density of electron state (DOS) were analyzed and compared. On the basis of the calculated results of EO/TM-doped $\text{Zn}_{12}\text{O}_{12}$ adsorbed complexes, we theoretically predicted that Cr- and V-doped $\text{Zn}_{12}\text{O}_{12}$ are suitable candidates for design and fabrication of sensing devices for detection of EO gas molecules, even in low concentration.

2 Computational studies

All the calculations were performed using Gaussian 09 program package (Frisch et al., 2013) at the level of DFT with B3LYP/6-31G (d) (Becke, 3-parameter, Lee-Yang-Parr) (Becke, 1988; Lee et al., 1988). For Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu atoms, the standard LANL2DZ (Los Alamos National Laboratory (LANL) including double-zeta (DZ)) basis set was used. Convergence of calculations was checked by comparison of the maximum energy and maximum displacement with the corresponding threshold values (Ha and $(1 \times 10^{-6}$ Ha and 6×10^{-4} Å, respectively). The DOS for all the studied structures was plotted by the Gauss Sum 2.1.4 program (O'boyle et al., 2008). The E_{ad} is defined as follows:

$$E_{\text{ad}} = E_{(\text{EO/nanocluster})} - (E_{\text{nanocluster}} + E_{\text{EO}}) + E_{\text{BSSE}} \quad (1)$$

where $E_{(\text{EO/nanocluster})}$, $E_{\text{nanocluster}}$ and E_{EO} are respectively correspond to energy of the adsorbed complexes, $\text{Zn}_{12}\text{O}_{12}$ nanocluster and EO molecule. The obtained negative values of E_{ad} indicated exothermic nature of the adsorption process for all the studied adsorbed complex systems. The calculated E_{ad} values have been corrected by the basis set superposition error (BSSE) using the counter-poise (CP) correction (Boys and Bernardi, 1970). The charge transfer between EO molecule and the adsorbents (i.e., pristine and TM-doped $\text{Zn}_{12}\text{O}_{12}$) was calculated by Mulliken charge analysis from the difference of charge concentration on EO before and after the adsorption.

The band-gap energy ($E_g = E_{\text{LUMO}} - E_{\text{HOMO}} = -(A - I)$) and the global hardness ($\eta = (I - A)/2$), where LUMO, HOMO, A and I refer respectively to the lowest unoccupied molecular orbital, highest occupied molecular orbital, electron affinity of molecule and ionization potential (Chattaraj et al., 2006; Koopmans, 1934; Phillips, 1961). The sensitivity of the pristine and TM-doped $\text{Zn}_{12}\text{O}_{12}$ for detection of EO was evaluated by calculation of % in following form:

$$\Delta E_g \% = [(E_{g2} - E_{g1}) / E_{g1}] \times 100 \quad (2)$$

where E_{g1} and E_{g2} are E_g values before and after adsorption of EO molecules.

3 Results and discussion

3.1 EO adsorption on pristine $\text{Zn}_{12}\text{O}_{12}$

As shown in Figure 1, the structural geometry of pristine $\text{Zn}_{12}\text{O}_{12}$ has been made of eight hexagons (B_{66}) and six tetragons (B_{46}) with tetrahedral rotational symmetry with inversion symmetry. The calculated average bond lengths of the B_{66} (D_1) and B_{46} (D_2) were about 1.85 and 1.93 Å, respectively (Table 1). The angles in tetragons (A_1 , A_2) and hexagons (A_3 , A_4) were 91.97, 86.92, 126.41 and 112.37 degree, respectively. Recently, the optimized structure of $\text{Zn}_{12}\text{O}_{12}$ using DFT/B3LYP with 6-31G (d) for oxygen and LANL2DZ for zinc showed that the distances D_1 and D_2 were 1.91 and 1.99 Å, respectively (de Oliveira et al., 2015). The calculated A_1 , A_2 , A_3 and A_4 angles in this work were obtained to be 90.8, 88.9, 123.6 and 116.2 degree, respectively. From the comparison, we concluded that the results are in good agreement with

Figure 1: (a) Optimized structure of $\text{Zn}_{12}\text{O}_{12}$, D and A means distance and angle, respectively; (b) Optimized structure of $\text{EO}/\text{Zn}_{12}\text{O}_{12}$; (c) DOS, HOMO and LUMO profiles of pristine $\text{Zn}_{12}\text{O}_{12}$; (d) DOS, HOMO and LUMO profiles of $\text{EO}/\text{Zn}_{12}\text{O}_{12}$; (e) Calculated electrostatic potential on the molecular surface of $\text{Zn}_{12}\text{O}_{12}$. Color ranges, in a.u.: blue, more positive than 0.0054; green, between 0.0054 and 0; yellow, between 0 and -0.0206; red, more negative than -0.0206.

Table 1: The bond lengths of the B_{66} (D_1) and B_{46} (D_2) and the angles A_1 , A_2 , A_3 and A_4 in the surface of pristine and TM-doped $\text{Zn}_{12}\text{O}_{12}$.

System	D_1 (Å)	D_2 (Å)	A_1 (deg)	A_2 (deg)	A_3 (deg)	A_4 (deg)
$\text{Zn}_{12}\text{O}_{12}$	1.85	1.93	91.97	86.92	126.41	112.37
Sc-doped $\text{Zn}_{12}\text{O}_{12}$	1.94	1.98	91.91	89.07	123.69	121.27
Ti-doped $\text{Zn}_{12}\text{O}_{12}$	1.84	1.86	90.59	88.38	129.32	104.57
V-doped $\text{Zn}_{12}\text{O}_{12}$	1.78	1.85	93.14	87.07	127.62	106.08
Cr-doped $\text{Zn}_{12}\text{O}_{12}$	1.76	1.87	90.05	88.77	129.69	103.99
Mn-doped $\text{Zn}_{12}\text{O}_{12}$	1.81	1.89	90.20	89.61	128.55	103.82
Fe-doped $\text{Zn}_{12}\text{O}_{12}$	1.81	1.87	90.50	89.88	127.15	118.11
Co-doped $\text{Zn}_{12}\text{O}_{12}$	1.82	1.86	90.71	88.64	127.75	107.21
Ni-doped $\text{Zn}_{12}\text{O}_{12}$	1.86	1.89	90.61	89.44	127.39	106.80
Cu-doped $\text{Zn}_{12}\text{O}_{12}$	1.85	1.89	90.78	88.49	126.87	107.18

the calculated data reported in the literature (de Oliveira et al., 2015).

For better understanding of the effect of EO adsorption on the electronic property of $\text{Zn}_{12}\text{O}_{12}$, DOS plots of the $\text{EO}/\text{Zn}_{12}\text{O}_{12}$ adsorbed complex were calculated

and analyzed. The energy values of HOMO and LUMO were obtained to be -6.99 and -2.86 eV, resulting in $E_g = 4.13$ eV. In accordance with the DOS plots as shown in Figure 1, the HOMO and LUMO respectively are more localized on the O and Zn atoms. Therefore, it is clear

that the Zn atoms are suitable sites for adsorption of EO molecules. On the other hand, in the most stable structure of EO/Zn₁₂O₁₂ adsorbed complex, O atom of EO molecule was attracted by Zn atom of Zn₁₂O₁₂. As shown by the MEP of Zn₁₂O₁₂ in Figure 1, it can be seen that the negative regions above the O atoms (red colors) are stronger than the positive ones of the Zn atoms (blue colors).

The optimized geometry structure of EO/Zn₁₂O₁₂ adsorbed complex is shown in Figure 1. The newly formed O–Zn bond and calculated adsorption energy were about 2.81 Å and -16.04 kcal/mol, respectively. The interaction between EO and Zn₁₂O₁₂ surface showed a charge transfer of -0.14 e from Zn₁₂O₁₂ to EO molecule. As show in Table 2, after the adsorption of EO molecule on Zn₁₂O₁₂, its electronic properties including HOMO, LUMO, and E_g were not significantly changed (4.13 to 4.15 eV). Therefore, it can be concluded that pristine Zn₁₂O₁₂ is not notably sensitive to the adsorption and detection of EO molecules.

3.2 EO adsorption on the TM-doped Zn₁₂O₁₂

To tailor the sensitivity and sensing range of doped Zn₁₂O₁₂ toward EO molecule, a Zn atom was replaced by different TM including Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and

Cu. The optimized structures are shown in Figure 2. The geometrical parameters (i.e., bond lengths and angles) of the TM-doped Zn₁₂O₁₂ showed in the Table 1.

After the doping process, the HOMO level was significantly shifted to higher energies, and consequently, the E_g was considerably narrowed. As shown in Table 2, in the case of Cr- and V-doped Zn₁₂O₁₂, the HOMO was increased from -6.99 to -3.99 and -5.20 eV, narrowing the E_g by about 2.93 and 1.81 eV, respectively. Similar trend was found for the other TM-doped Zn₁₂O₁₂. As shown, upon doping of the TM, E_g values of Zn₁₂O₁₂ were decreased from 4.13 eV in pristine Zn₁₂O₁₂ to 3.70-1.13 eV in the doped forms. The molecules having small E_g value and excitation energy which are known as soft molecules are more polarizable. Therefore, the soft molecules show electron density changes more easily than hard molecules with high E_g value, leading to higher chemical reactivity. According to the calculated η, the order of systems reactivity of the studied systems was as follows:

Sc-doped Zn₁₂O₁₂ > Cr-doped Zn₁₂O₁₂ > Ti-doped Zn₁₂O₁₂ > V-doped Zn₁₂O₁₂ > Mn-doped Zn₁₂O₁₂ > Fe-doped Zn₁₂O₁₂ > Ni-doped Zn₁₂O₁₂ > Co-doped Zn₁₂O₁₂ > Cu-doped Zn₁₂O₁₂.

The optimized structures of EO molecule adsorbed on the surface of TM-doped Zn₁₂O₁₂ from its O atom are

Table 2: The calculated E_{ad} (kcal/mol), HOMO, LUMO, E_f and E_g (eV) for the studied systems. The average total Mulliken charge transfer from the adsorbents to EO molecule (Q_t). The nearest atom-to-atom distance between the O atom of EO, X (X = Zn, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) of pristine and TM-doped Zn₁₂O₁₂ (Å) and their E_g change (ΔE_g) values after the EO adsorption.

System	E _{ad}	d _{X-O} (Å)	Q _t (e)	E _{HOMO}	E _{LUMO}	E _g	E _f	η	ΔE _g %
Zn ₁₂ O ₁₂	–	–	–	-6.99	-2.86	4.13	-4.93	2.07	–
EO/Zn ₁₂ O ₁₂	-16.04	2.81	-0.14	-6.67	-2.52	4.15	-4.60	2.08	0.48
Sc-doped Zn ₁₂ O ₁₂	–	–	–	-3.65	-2.52	1.13	-3.09	0.57	–
EO/Sc-doped Zn ₁₂ O ₁₂	-19.92	2.23	-0.15	-3.68	-2.51	1.17	-3.10	0.59	3.53
Ti-doped Zn ₁₂ O ₁₂	–	–	–	-4.05	-2.83	1.22	-3.44	0.61	–
EO/Ti-doped Zn ₁₂ O ₁₂	-20.55	2.22	-0.16	-4.00	-2.74	1.26	-3.37	0.63	3.28
V-doped Zn ₁₂ O ₁₂	–	–	–	-5.20	-2.88	2.32	-4.04	1.16	–
EO/V-doped Zn ₁₂ O ₁₂	-36.65	2.00	-0.18	-5.62	-2.64	2.98	-4.13	1.49	28.45
Cr-doped Zn ₁₂ O ₁₂	–	–	–	-3.99	-2.79	1.20	-3.39	0.60	–
EO/Cr-doped Zn ₁₂ O ₁₂	-60.04	1.97	-0.19	-3.83	-2.12	1.71	-2.98	0.86	42.50
Mn-doped Zn ₁₂ O ₁₂	–	–	–	-5.03	-2.67	2.36	-3.85	1.18	–
EO/Mn-doped Zn ₁₂ O ₁₂	-31.91	2.01	-0.15	-4.99	-2.51	2.48	-3.75	1.24	5.08
Fe-doped Zn ₁₂ O ₁₂	–	–	–	-4.92	-2.53	2.39	-3.73	1.20	–
EO/Fe-doped Zn ₁₂ O ₁₂	-35.98	2.00	-0.16	-5.18	-2.38	2.80	-3.78	1.40	17.15
Co-doped Zn ₁₂ O ₁₂	–	–	–	-5.71	-2.34	3.37	-4.03	1.69	–
EO/Co-doped Zn ₁₂ O ₁₂	-31.11	2.02	-0.15	-5.82	-2.27	3.55	-4.05	1.78	5.34
Ni-doped Zn ₁₂ O ₁₂	–	–	–	-5.75	-2.71	3.04	-4.23	1.52	–
EO/Ni-doped Zn ₁₂ O ₁₂	-33.31	2.01	-0.17	-5.54	-2.33	3.21	-3.94	1.61	5.59
Cu-doped Zn ₁₂ O ₁₂	–	–	–	-6.48	-2.78	3.70	-4.63	1.85	–
EO/Cu-doped Zn ₁₂ O ₁₂	-29.21	2.05	-0.16	-6.46	-2.64	3.82	-4.55	1.91	3.24

Figure 2: Optimized structures of TM-doped $\text{Zn}_{12}\text{O}_{12}$ and their adsorbed complexes with EO molecule. Distances are in Å.

shown in Figure 2. In order to consider the influence of doping on the electronic properties of $\text{Zn}_{12}\text{O}_{12}$, the DOS plots of Cr-doped $\text{Zn}_{12}\text{O}_{12}$, V-doped $\text{Zn}_{12}\text{O}_{12}$, EO/Cr-doped $\text{Zn}_{12}\text{O}_{12}$ and EO/V-doped $\text{Zn}_{12}\text{O}_{12}$ were calculated and the results of Cr- and V-doped $\text{Zn}_{12}\text{O}_{12}$ and respective adsorbed complex were presented in Figure 3. As shown in this figure, in the EO/Cr-doped $\text{Zn}_{12}\text{O}_{12}$ and EO/V-doped $\text{Zn}_{12}\text{O}_{12}$ adsorbed complexes, the HOMO levels of Cr- and V-doped $\text{Zn}_{12}\text{O}_{12}$ were shifted closer to the EO molecule. Furthermore, without the doping, from the DOS plots as shown in Figure 1, it was clearly visible that the DOS of $\text{Zn}_{12}\text{O}_{12}$ near the Fermi levels (E_f) showed no distinct changes after adsorption of EO molecules, while for the EO/Cr-doped $\text{Zn}_{12}\text{O}_{12}$ and EO/V-doped $\text{Zn}_{12}\text{O}_{12}$, the DOSs was shifted to more negative energies near the Fermi

level, indicating a relative strength molecular interaction. In summary, as shown in Table 2, the doping with Sc, Ti and Cu atoms did not show a significant change on E_g value of the corresponding doped $\text{Zn}_{12}\text{O}_{12}$. However, the doping with Mn, Fe, Co, and Ni atoms revealed slightly improvement on the sensitivity of the respective doped $\text{Zn}_{12}\text{O}_{12}$ towards EO molecules.

The gas sensor performance is generally influenced by changes in electrical conductivity ($\Delta\sigma$) of adsorbent materials after exposing gas molecules. The electrical conductivity (σ) at a given temperature (T) can be related to the E_g values according to: $\sigma = A T^{3/2} \exp(-E_g/2kT)$, where k is the Boltzmann's constant and A (electrons/ $\text{m}^3\text{K}^{3/2}$) is a constant (Li, 2006). According to the above relation, after the adsorption of EO molecule, the observed E_g

Figure 3: (a) DOS, HOMO and LUMO profiles of V-doped $\text{Zn}_{12}\text{O}_{12}$ and EO/V-doped $\text{Zn}_{12}\text{O}_{12}$; (b) DOS, HOMO and LUMO profiles of Cr-doped $\text{Zn}_{12}\text{O}_{12}$ and EO/Cr-doped $\text{Zn}_{12}\text{O}_{12}$.

change induces a change in the σ values, which then generates a recordable electric signal (Beheshtian et al., 2011; Beheshtian et al., 2013b; Soltani et al., 2013).

The E_g of Cr- and V-doped $\text{Zn}_{12}\text{O}_{12}$ was significantly changed after the adsorption of EO (i.e., $\Delta E_g = 42.50$ and 28.45%, respectively). Based on the highest ΔE_g % values, it can be concluded that Cr- and V-doped $\text{Zn}_{12}\text{O}_{12}$ have promising capability to be applied for fabrication of a favorable gas sensor for detection of EO molecules. In the practical performance of gas sensors, the recovery time (τ) is another important parameter for the practical applications, which should be as small as possible for device reusability. The τ can be expressed using the conventional transition state theory as: $\tau = \vartheta_0^{-1} \exp\left[-\frac{E_{\text{ad}}}{kT}\right]$, where ϑ_0 is the attempt frequency. Therefore, the more negative value of E_{ad} can postpone the sensor recovery time in an exponential manner. However, the calculated E_{ad} of EO/Cr-doped $\text{Zn}_{12}\text{O}_{12}$ and EO/V-doped $\text{Zn}_{12}\text{O}_{12}$ were not too large to hinder the recovery in a reasonable time.

The minimum atom-to-atom distance between the O atom of EO molecule with the Cr and V atoms of Cr- and V-doped $\text{Zn}_{12}\text{O}_{12}$ in the EO/Cr-doped $\text{Zn}_{12}\text{O}_{12}$ and EO/V-doped

$\text{Zn}_{12}\text{O}_{12}$ adsorbed complexes was obtained to be 1.97 and 2.00 Å, respectively and was shorter than of the other adsorbed systems (Table 2). After adsorption of electrophilic or nucleophilic molecular species on an absorbent surface, a charge transfer is expected to occur from the electron donor to electron acceptor (e.g., from the pristine and doped $\text{Zn}_{12}\text{O}_{12}$ to EO). Therefore, the Mulliken charge analysis of the TM-doped $\text{Zn}_{12}\text{O}_{12}$ has been performed to evaluate their *electron donor*-ability. The calculated Q_T values for Cr-, V-, Ni-, Fe-, Cu-, Ti-, Co-, Mn-, Sc-doped $\text{Zn}_{12}\text{O}_{12}$ systems obtained to be -0.40, -0.38, -0.20, -0.18, -0.09, -0.09, -0.08, -0.04 and -0.06 e. This revealed that among the doped atoms, Cr and V atoms in the Cr- and V-doped $\text{Zn}_{12}\text{O}_{12}$ show a higher charges transfer tendency to their adjacent oxygen atoms, indicating a *higher electron donor*-ability. For the adsorbed complexes, as shown in Table 2, the highest Q_T values were, as expected, -0.19 and -0.18 e, respectively for the EO/Cr-doped $\text{Zn}_{12}\text{O}_{12}$ and EO/V-doped $\text{Zn}_{12}\text{O}_{12}$ systems, indicating stronger interaction between the doped Cr and V atoms and oxygen atoms of EO molecules due to the more charge transfers. For the other TM-doped $\text{Zn}_{12}\text{O}_{12}$, the calculated charge transfer was obtained to be in range of -0.14 to -0.17 e.

The E_{ad} of EO molecule on the TM-doped $Zn_{12}O_{12}$ was in the following order: EO/Cr-doped $Zn_{12}O_{12}$ (-60.04) > EO/V-doped $Zn_{12}O_{12}$ (-36.65) > EO/Fe-doped $Zn_{12}O_{12}$ (-35.98) > EO/Ni-doped $Zn_{12}O_{12}$ (-33.31) > EO/Mn-doped $Zn_{12}O_{12}$ (-31.91) > EO/Co-doped $Zn_{12}O_{12}$ (-31.11) > EO/Cu-doped $Zn_{12}O_{12}$ (-29.21) > EO/Sc-doped $Zn_{12}O_{12}$ (-19.92) > EO/Ti-doped $Zn_{12}O_{12}$ (-16.04) kcal/mol. According to the obtained results, the E_{ad} values were negative for all systems which indicate an exothermic adsorption process. As shown in Table 2, the E_{ad} value in EO/Cr-doped $Zn_{12}O_{12}$ and EO/V-doped $Zn_{12}O_{12}$ is -60.04 and -36.65 kcal/mol, respectively, indicating a strong interaction with EO molecule.

Ultimately, according to the consistent computational results of Mulliken charge, E_{ad} , atom-to-atom distance, DOS plot, $\Delta E_g\%$ and HOMO–LUMO orbital analysis, Cr- and V-doped $Zn_{12}O_{12}$ can be considered as potential material for adsorption and detection of EO molecules.

4 Conclusion

In the present work, we have investigated the electronic sensitivity and reactivity of pristine and TM-doped $Zn_{12}O_{12}$ to EO molecule using the DFT method. The calculated DOS of the adsorbed complexes indicated the strong interaction between Cr- and V-doped $Zn_{12}O_{12}$ and EO molecules. According to the results, the highest Q_T values were obtained to be -0.19 and -0.18 e, respectively for Cr- and V-doped $Zn_{12}O_{12}$ to EO molecule. Among the TM-doped $Zn_{12}O_{12}$, Cr-doped $Zn_{12}O_{12}$ with the calculated $\Delta E_g\%$ of 42.50% and E_{ad} of -60.04 kcal/mol and V-doped $Zn_{12}O_{12}$ with the obtained $\Delta E_g\%$ of 28.45% and E_{ad} of -36.65 kcal/mol showed superior sensitivity toward EO molecules. The computational results of two important key-characters of gas sensor devices (i.e., ΔE_g and the resultant $\Delta\sigma$, as well as τ) indicated that the TM-doped $Zn_{12}O_{12}$ especially Cr- and V-doped $Zn_{12}O_{12}$ can be used to develop the new generation of sensitive, accurate and portable gas sensor devices.

Acknowledgments: The authors appreciate the partial financial support of this study by university of Kashan, Iran.

References

Afshari T., Mohsennia M., Effect of external electric field on the adsorption of ethylene oxide on pristine and Al-doped coronenes: A DFT study. *J. Theor. Comput. Chem.*, 2018, 17:1850032-1850043.

- Alver Ö., Parlak C., Ramasami P., Şenyel M., Interaction between doped C_{60} fullerenes and piperazine-2, 3, 5, 6-tetraone: DFT simulation. *Main Group Met. Chem.*, 2018, 41, 63-6.
- Aslanzadeh S., Transition metal doped ZnO nanoclusters for carbon monoxide detection: DFT studies. *J. Mol. Model.*, 2016, 22, 160-165.
- Bashir R., Afroze B., Zulfiqar H.F., Saleem R., Altaf I., Saleem F., et al., Microbiological Load of Ethylene Oxide Sterilized Medical Devices and its Elimination by Cobalt 60 Source. *J. Coll. Physicians Surg. Pak.*, 2016, 26, 486-489.
- Becke A.D., Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, 1988, 38, 3098-3100.
- Beheshtian J., Kamfiroozi M., Bagheri Z., Ahmadi A., Computational study of CO and NO adsorption on magnesium oxide nanotubes. *Physica E*, 2011, 44, 546-549.
- Beheshtian J., Peyghan A.A., Bagheri Z., Detection of phosgene by Sc-doped BN nanotubes: a DFT study. *Sensor. Actuator. B-Chem.*, 2012a, 171, 846-852.
- Beheshtian J., Peyghan A.A., Bagheri Z., Nitrate adsorption by carbon nanotubes in the vacuum and aqueous phase. *Monatsh. Chem.*, 2012b, 143, 1623-1626.
- Beheshtian J., Peyghan A.A., Bagheri Z., Ab initio study of NH_3 and H_2O adsorption on pristine and Na-doped MgO nanotubes. *Struct. Chem.*, 2013a, 24, 165-170.
- Beheshtian J., Peyghan A.A., Noei M., Sensing behavior of Al and Si doped BC_3 graphenes to formaldehyde. *Sensor. Actuator. B-Chem.*, 2013b, 181, 829-834.
- Boys S.F., Bernardi F.D., The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol. Phys.*, 1970, 19, 553-566.
- Capone S., Forleo A., Francioso L., Rella R., Siciliano P., Spadavecchia J., et al., Solid state gas sensors: state of the art and future activities. *J. Optoelectron. Adv. M.*, 2003, 5, 1335-1348.
- Chattaraj P.K., Sarkar U., Roy D.R., Electrophilicity index. *Chem. Rev.*, 2006, 106, 2065-2091.
- Degler D., Barz N., Dettinger U., Peisert H., Chassé T., Weimar U., et al., Extending the toolbox for gas sensor research: Operando UV/vis diffuse reflectance spectroscopy on SnO_2 -based gas sensors. *Sensor. Actuator. B-Chem.*, 2016, 224, 256-259.
- de Oliveira O.V., Pires J.M., Neto A.C., dos Santos J.D., Computational studies of the $Ca_{12}O_{12}$, $Ti_{12}O_{12}$, $Fe_{12}O_{12}$ and $Zn_{12}O_{12}$ nanocage clusters. *Chem. Phys. Lett.*, 2015, 634, 25-28.
- Duan J., Huang X., Wang E., PEG-assisted synthesis of ZnO nanotubes. *Mater. Lett.*, 2006, 60, 1918-1921.
- Epifani M., Comini E., Díaz R., Genç A., Andreu T., Siciliano P., et al., Acetone sensors based on TiO_2 nanocrystals modified with tungsten oxide species. *J. Alloy. Compd.*, 2016, 665, 345-351.
- Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., et al., Gaussian 09, Revision D.01, Gaussian, Inc. Wallingford, CT, 2013.
- Gong H., Hu J. Q., Wang J.H., Ong C.H., Zhu F.R., Nano-crystalline Cu-doped ZnO thin film gas sensor for CO. *Sensor. Actuator. B-Chem.*, 2006, 115, 247-251.
- Hadipour N.L., Ahmadi Peyghan A., Soleymanabadi H., Theoretical study on the Al-doped ZnO nanoclusters for CO chemical sensors. *J. Phys. Chem. C*, 2015, 119, 6398-6404.

- Ivanov V.A., Aminov T.A., Novotortsev V.M., Kalinnikov V.T., Spintronics and spintronics materials. *J. Russ. Chem. Bull. Int. Ed.*, 2004, 53, 2357-2405.
- Kakemam J., Peyghan A.A., Electronic, energetic, and structural properties of C- and Si-doped $\text{Mg}_{12}\text{O}_{12}$ nano-cages. *Comp. Mater. Sci.*, 2013, 79, 352-355.
- Kaushik A., Dalela B., Kumar S., Alvi P.A., Dalela S., Role of Co doping on structural, optical and magnetic properties of TiO_2 . *J. Alloy. Compd.*, 2013, 552, 274-278.
- Kerkez Ö., Boz İ., Photo (electro) catalytic activity of Cu^{2+} -modified TiO_2 nanorod array thin films under visible light irradiation. *J. Phys. Chem. Solids*, 2014, 75, 611-618.
- Kim S., Park S., Park S., Lee C., Acetone sensing of Au and Pd-decorated WO_3 nanorod sensors. *Sensor. Actuator. B-Chem.*, 2015, 209, 180-185.
- Koopmans T., Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den einzelnen Elektronen eines Atoms. *Physica*, 1934, 1, 104-113.
- Lahmer M.A., The effect of hydrogen adsorption on the properties of undoped and Cu doped ZnO (100) surfaces: A first-principles study. *J. Phys. Chem. Solids*, 2016, 89, 89-96.
- Lee C., Yang W., Parr R.G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, 1988, 37, 785-789.
- Li S.S., *Semiconductor Physical Electronics* (2nd ed.). Springer, USA, 2006.
- Mahdavian L., Simulation of SnO_2/WO_3 nanofilms for alcohol of gas sensor based on metal dioxides: MC and LD studies. *J. Nanostruct. Chem.*, 2012, 3, 1.
- Marcel H.F.S., Kawazoe Y., Sharma P., Inoue A., Raju A.R., Rout C., et al., First principles based design and experimental evidence for a ZnO-based ferromagnet at room temperature. *Phys. Rev. Lett.*, 2005, 94, 187204-187207.
- Mohsennia M., Rakhshi M., Rasa H., A computational study on interactions of Ni- and Pt-doped boron nitride nano tubes with NH_3 in presence and absence of electric fields. *Comput. Theor. Chem.*, 2018, 1136, 1-9.
- O'boyle N.M., Tenderholt A.L., Langner K.M., CcLib: a library for package-independent computational chemistry algorithms. *J. Comput. Chem.*, 2008, 29, 839-845.
- Özgür Ü., Alivov Y.I., Liu C., Teke A., Reshchikov M., Doğan S., et al., A comprehensive review of ZnO materials and devices. *J. Appl. Phys.*, 2005, 98, 041301.
- Peyghan A.A., Noei M., Electronic Response of Nano-sized Cages of ZnO and MgO to Presence of Nitric Oxide. *Chin. J. Chem. Phys.*, 2013, 26, 231-236.
- Peyghan A.A., Noei M., The alkali and alkaline earth metal doped ZnO nanotubes: DFT studies. *Phys. B-Condens. Mat.*, 2014, 432, 105-110.
- Peyghan A.A., Yourdkhani S., Capture of carbon dioxide by a nanosized tube of BeO: a DFT study. *Struct. Chem.*, 2014, 25, 419-426.
- Peyghan A.A., Laeen S.P., Aslanzadeh S.A., Moradi M., Hydrogen peroxide reduction in the oxygen vacancies of ZnO nanotubes. *Thin Solid Films*, 2014, 556, 566-570.
- Peyghan A.A., Rastegar S.F., Bagheri Z., Selective detection of F_2 in the presence of CO , N_2 , O_2 , and H_2 molecules using a ZnO nanocluster. *Monatsh. Chem.*, 2015, 146, 1233-1239.
- Phillips J.C., Generalized Koopmans' Theorem. *Phys. Rev.*, 1961, 123, 420-424.
- Rakhshi M., Mohsennia M., Rasa H., Sameti M.R., First-principle study of ammonia molecules adsorption on boron nitride nanotubes in presence and absence of static electric field and ion field. *Vacuum*, 2018, 155, 456-464.
- Rebbsdat S., Mayer D., Wiley-VCH Verlag GmbH & Co. KGaA, 2001.
- Rezaei-Sameti M., Yaghoobi S., Theoretical study of adsorption of CO gas on pristine and AsGa-doped (4, 4) armchair models of BPNTs. *Comput. Condens. Matter*, 2015, 3, 21-29.
- Sahay P.P., Nath R.K., Al-doped ZnO thin films as methanol sensors. *Sensor. Actuator. B-Chem.*, 2008, 134, 654-659.
- Samadzadeh M., Rastegar S.F., Peyghan A.A., The electronic response of nano-sized tube of BeO to CO molecule: a density functional study. *Struct. Chem.*, 2015, 26, 809-814.
- Soltani A., Peyghan A.A., Bagheri Z., H_2O_2 adsorption on the BN and SiC nanotubes: a DFT study. *Physica E*, 2013, 48, 176-180.
- Steenland K., Stayner L., Greife A., Halperin W., Hayes R., Hornung R., et al., Mortality among workers exposed to ethylene oxide. *New Engl. J. Med.*, 1991, 324, 1402-1407.
- Yang Y.A., Yao J.N., Microstructural properties of an electrochromic WO_3 thin film. *J. Phys. Chem. Solids*, 2000, 61, 647-650.
- Yoon H.J., Yang J. H., Zhou Z., Yang S.S., Cheng M.M.C., Carbon dioxide gas sensor using a graphene sheet. *Sensor. Actuator. B-Chem.*, 2011, 157, 310-313.
- Zhu G., Xu H., Liu Y., Xu X., Ji Z., Shen X., et al., Enhanced gas sensing performance of Co-doped ZnO hierarchical microspheres to 1, 2-dichloroethane. *Sensor. Actuator. B-Chem.*, 2012, 166, 36-43.
- Ziat Y., Benyoussef A., El Kenz A., Magnetic and electronic properties of Cr- and Mn-doped SnO_2 : ab initio calculations. *J. Phys. Chem. Solids*, 2014, 75, 701-709.