Associative and Dissociative Adsorption of N₂O Molecule Over C₂₄ Fullerene Doped With V, Mn, Ru, Pd and Rh: A DFT Investigation

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Research Article

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Abstract

DFT calculations using the PBE-D3 level of theory were conducted on the C_{24} and MC_{23} ($M = V, Mn, Ru, Pd, Rh$ and Au) clusters in order to determine their stability and electronic and magnetic properties. The interaction of the N_2O molecule with the above clusters has also been examined in order to assess their adsorption and catalytic properties. The results show that the reactivity of the C_{24} fullerene was greatly improved after doping with a TM atom, and the metal atom which was replaced the carbon atom in the pure C_{24} fullerene is considered as the most favorable site to adsorb and dissociate the N_2O molecule. The molecular adsorption of the N_2O on the surface of the MC_{23} clusters from its oxygen atom was found to be less energetically favorable than by nitrogen atom, and the calculated adsorption energies (E_{ads}) are in the range of - 6.5 to - 24.7 kcal mol⁻¹. The N_2O adsorption on the metal site of the clusters could also lead to the dissociation of the N_2O into O^* and N_2 molecule with adsorption energies which vary from - 2.3 to - 86.8 kcal mol⁻¹. The mechanism of the N_2O dissociation on the clusters surface was studied, and the activation energies for each system were calculated in order to find the most catalytically active clusters in the N_2O decomposition. The results indicate that the activation energies of the VC_{23} and MnC_{23} clusters are much lower than those obtained for the other clusters, reflecting high catalytic activity of the two clusters in the N_2O decomposition reaction compared to the other studied clusters. The values of E_{ac} of the reaction over the VC_{23} and MnC_{23} cluster are 9.3 and 7.9 kcal mol⁻¹, respectively, indicating that both clusters could be employed as greatly active and efficient nanocatalysts for the N_2O decomposition reaction.

1. Introduction

Nitrous oxide (N_2O) is considered as a substantial greenhouse gas, which contributes significantly to the destruction of the stratospheric ozone layer [1–2]. Thus, the catalytic N_2O elimination to its elements is an important subject for environmental catalysis [3–8]. It was found that the simplest way to eliminate N_2O gas is its decomposition into nitrogen and oxygen over an active and efficient catalyst [9–13]. Also, if the concentration of N_2O in the atmosphere increases, it can cause serious hurt to the human environment. Therefore, the N_2O decomposition to nitrogen and oxygen gas is a best process to reduce environmental pollution.

Several supported catalysts, including metal oxides and transition metals prepared by the conventional method were tested in the N_2O decomposition reaction at different temperatures, and the obtained results show that the metal-based supported catalysts have a high reactivity compared to the other types of catalysts [6, 14–21]. Moreover, the reactivity of the catalyst in the decomposition of N_2O was greatly influenced by several parameters such as the method of preparation, the nature of support, the metal precursors and the dispersion of particles on the surface of the catalyst [9, 17, 22]. Yuzaki et al. [22] have investigated the effects of the support and the nature of metal precursors onto the catalytic activity of the Rh catalysts, and concluded that the reactivity of the catalyst in the N_2O decomposition is strongly related to the nature of the support. As result they found that the catalytic activity of the Rh/USY (ultrastable Y zeolite) and Rh/ Al_2O_3 catalysts in the N_2O dissociation is much higher than that obtained for the other supported catalysts (Rh/NaY, Rh/ ZrO_2 ,

Rh/CeO₂, Rh/La₂O₃ and Rh/FSM-16). Furthermore, the activity of the Rh catalyst prepared from Rh(NO₃)₂ was found to be much greater than that of the Rh catalyst obtained from RhCl₃. This large difference in activity was ascribed to the residual Cl remaining on the surface of the Rh catalyst prepared from RhCl₃, which mainly contributes to the inhibition of the reaction. The results obtained by them show also that the catalytic activity of the catalysts was slightly reduced by the addition of oxygen. A series of Ru catalysts with Ru loading between 0.5 and 10 wt.% were prepared by classical method and their reactivity was evaluated in the N₂O decomposition at temperatures which vary between 300°C and 450°C [23]. The results clearly reveal that the catalyst activity depends considerably on the Ru loading, and the maximum activity obtained was assigned to the Ru/MCM-41 catalyst which has a Ru loading of 5.0 wt.%. The influence of CO over the N₂O decomposition reaction in the presence of the Ru catalysts has also been investigated, and the results indicate that the addition of the CO molecule in the reaction mixture enhance considerably the N₂O conversion, and a total conversion of N₂O is achieved at lower temperature (around 300°C). Without CO gas, the total conversion was reached at temperatures above 380°C. The catalytic activity of four types of manganese oxides (MnO, Mn₂O₃, Mn₃O₄, MnO₂) was examined in the decomposition of N₂O by Yamashita et al. [24], and the obtained results show that the highest reactivity and the stable behavior has been observed for the Mn₂O₃ catalyst. The presence of O₂ in the system inhibits the N₂O decomposition, whereas the addition of N₂ has no effect on the activity of the catalysts. The activation energy of the rate-determining step was found to be 31 kcal mol⁻¹. The nanocatalysts with the particle sizes which vary between 2 and 8 nm were synthesized by simple chemical method at lower temperatures, and then their reactivity was evaluated in the N₂O dissociation reaction [4–5, 25]. These nanoparticles show high activity and stability in the above reaction compared to those obtained by classical method. For example, the nano-Ag/SiO₂ catalyst prepared by radiolysis method (Ag-Rad) were tested in the decomposition of N₂O at different temperatures, and the results obtained are compared to typical catalyst prepared by impregnation method (Ag-Imp) [4]. The N₂O conversion for the Ag-Rad nanocatalyst was found to be almost 2 times higher than that of the Ag-Imp catalyst, and the selectivity to N₂ gas for the Ag-Rad nanocatlyst is nearly double compared with that of the Ag-Imp catalyst.

Theoretically, the adsorption and dissociation of N₂O over the surface of the catalysts were mainly studied by using the DFT calculations [26–30]. For example, Sun et al. [27] investigated the adsorption and decomposition of the N₂O molecule over the Cu₂O (111) surface, and the results reported by them show that the N₂O molecule prefers to adsorb on the Cu site as a first step, and then breaks down readily on this metal site as a second step with an activation energy and reaction energy of 61.2 and 18.5 kcal mol⁻¹, respectively. The adsorption and dissociation of N₂O were investigated over the Rh_n (n = 1–6) nanoclusters by Rodriguez-Kessler et al. [26], and the results reveal that the adsorption energy increases with increasing cluster size and the calculated E_{ads} values range from – 50.7 to – 75.6 kcal mol⁻¹. Furthermore, the dissociation of N₂O over the Rh_{1–4} nanoclusters was found more energetically favorable than on their neighboring clusters. Baei et al. [28] have studied the adsorption of N₂O onto the pristine and Si-doped BN nanocage by DFT calculations at the B3LYP/31G* level of theory. The obtained results indicated that the N₂O was physically adsorbed on the surface of the BN nanocage, while the O atom of N₂O was strongly bonded with the Si site of the Si-doped BN nanocluster with an adsorption energy of – 67.2 kcal mol⁻¹. Recently, Zhang et al. studied the interaction of the N₂O molecule with the TM (Mn, Fe, Co, Zn, Ni and Cu) cations-exchanged ZSM-5 by combination of the

theoretical and experimental methods [31]. The theoretical results reveal that the calculated E_{ads} of N_2O over TM cations followed the order: $\text{Fe} > \text{Mn} > \text{Co} > \text{Zn} > \text{Ni} > \text{Cu}$, which is consistent with the experimental results. DFT calculations indicate also that the adsorption of N_2O on TM active site through O-end of N_2O molecule is more energetically favorable than by N-end. The change in enthalpy (ΔH_{ads}) varies between -12.3 to -58.0 kcal mol^{-1} , proposing a strong interaction between both species. Moreover, it was noticed that the ΔH_{ads} increases with increasing of the amount of charge transferred from the N_2O molecule to the TM cations during the complexation process.

Fullerenes as nanomaterials of zero-dimensional show exceptional physical and chemical properties because of their small size. Doping of the nanomaterials with TM atoms could greatly improve their stability, electronic and catalytic properties. For example, the TM-doped fullerenes which were employed as catalytic nanomaterials have showed a great catalytic activity in many chemical reactions [32–33]. Fullerene was also employed as a nanomaterial for hydrogen storage, and its doping with alkali and alkaline-earth metal atoms can enhances its hydrogen storage capacity [34].

In the present work, we have investigated the associative and dissociative adsorption of N_2O molecule onto the surface of the C_{24} and MC_{23} ($\text{M} = \text{V}, \text{Pd}, \text{Rh}, \text{Ru}, \text{Au}$ and Mn) clusters using DFT calculations at the PBE-D3 level of theory. Based on the most stable configurations which were optimized, the stability, electronic and magnetic properties of the MC_{23} nanoclusters were calculated and discussed. The properties of the complexes formed by interaction of the above clusters with the N_2O molecule have also been predicted and analyzed. This work is organized as: “Computational methods” section gives a description of the computational method employed in this study to determine the reactivity, electronic and magnetic properties of the MC_{23} clusters. The results obtained on the adsorption properties of the N_2O molecule over the surface of the C_{24} and MC_{23} clusters were presented in “Results and discussion” section. Finally, the conclusions of this research paper were given in “Conclusions” section.

2. Computational Methods

In this work, the stability and electronic properties of the MC_{23} clusters and their interaction with the N_2O molecule were predicted using DFT calculations with the PBE functional including the Grimme dispersion correction (PBE-D3) as implemented in the Gaussian09 package [35]. Meanwhile, the LanL12DZ basis set was employed for the metal atoms ($\text{V}, \text{Mn}, \text{Ru}, \text{Pd}, \text{Rh}$ and Au), while the 6-311G (d,p) basis set has been used for the C, N and O atoms [36–38]. The LanL2DZ was indicated as an efficient basis set for the calculations of the properties of the systems containing transition metal atoms. For example, this basis set was successfully employed to investigate the structural and electronic properties of the Co-decorated C_{24} fullerene, and their interaction with the chemical warfare agents (Soman, sarin, chlorosaman and chlorosarin) [39]. The PBE method was also widely applied to study the stability, electronic and magnetic properties of the binary nanoclusters and their sensitivity toward toxic gas molecules [39–40]. The stability, electronic and adsorption properties of the MC_{23} clusters have also been calculated using the B3LYP method, and the predicted results were compared with those obtained from the PBE functional.

In order to measure the strength of the interaction between the cluster and the N₂O molecule in the complexes, the adsorption energy (E_{ads}) for each studied complex was calculated from the Eq. (1), and the values obtained could provide information on the nature of the interaction between both species (physical or chemical adsorption):

$$E_{\text{ads}} = E_{\text{N}_2\text{O}/\text{Cluster}} - (E_{\text{N}_2\text{O}} + E_{\text{Cluster}}) \quad (1)$$

where $E_{\text{N}_2\text{O}/\text{Cluster}}$ is the total energy of the adsorbed N₂O over the C₂₄ or MC₂₃ cluster. $E_{\text{N}_2\text{O}}$ and E_{Cluster} are the total energies of the N₂O molecule and the C₂₄ or MC₂₃ nanocluster, respectively.

Using the Koopmans theorem [41], the chemical hardness (η) and softness (s) have also been computed in our study in order to estimate the stability (reactivity) of the MC₂₃ clusters and their complexes formed by the N₂O adsorption over their surface. The values of the hardness and softness are estimated by using the following expressions:

$$\eta = E_{\text{L}} - E_{\text{H}} / 2 \quad (2)$$

$$s = 1 / 2 \eta \quad (3)$$

where E_{L} and E_{H} are the total energies of the LUMO and HOMO states of the nanoclusters.

The barrier energy (E_{a}) of the N₂O decomposition reaction is calculated from the difference between the total energies of the optimized configurations of the reactant and transition state. So, the E_{a} is given by the following equation:

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{R}} \quad (4)$$

where E_{TS} and E_{R} are the total energies of the optimized structures of the transition states and reactants, respectively.

The structures of the transition states (TS) for each studied system were predicted using the complete linear synchronous (LST)/quadratic synchronous transit (QST) calculations which are implemented in the Dmol³ package [42–43].

3. Results And Discussion

3.1 Electronic properties of the C₂₄ and MC₂₃ (M = V, Pd, Rh, Ru, Au and Mn) clusters

In this section, the stability, electronic and magnetic properties of the C₂₄ fullerene were investigated. Also, in order to evaluate the effect of the metal doping onto the reactivity, electronic, adsorption properties of the pure C₂₄ fullerene, a carbon atom of the C₂₄ fullerene has been substituted by a metal atom (V, Pd, Rh, Ru, Au or Mn). Doping of C₂₄ nanocage with transition metal atoms was found to be an excellent way to improve their electronic and catalytic properties. The geometries of the C₂₄, V-, Pd-, Rh-, Ru-, Au- and Mn-doped C₂₄ clusters were fully optimized by using DFT calculations at the PBE-D3 level of theory. Upon optimizations, the most

stable configurations of the seven nanoclusters and their structural parameters are shown in Fig. 1. The energies of HOMO and LUMO orbitals (E_H and E_L), energy gap (E_g), hardness (η), softness (s), charge on metal atom (q_M), dipole moment (β_T) and total magnetic moment (μ_T) of these clusters have been summarized in Table 1. For comparison, the configurations of the above clusters have also been optimized with the B3LYP-D3 method, and the results obtained were reported in parentheses in Table 1. As it was shown in the Fig. 1, two types of the C-C bonds in the C_{24} fullerene were predicted in our calculations; the first one is shared between hexagonal and hexagonal rings with a length of 1.38 Å, whereas the second one which was shared between hexagonal and tetragonal rings was found to be 1.50 Å. The C-C-C bond angle in the pure C_{24} cage with T_h symmetry was found to be 120°. When a carbon atom of the C_{24} nanocage was replaced by a V, Pd, Rh, Ru, Au or Mn atom, a slight deformation in the shape of the C_{24} fullerene was observed, in which the metal atom was pulled out of the surface of the nanocage (Fig. 1). Comparing with the calculated C-C bond lengths in the pure C_{24} nanocage, the M-C bond distances in the MC_{23} clusters are considerably elongated, and the calculated values of the M-C bond which was shared between hexagonal and tetragonal rings (hexagonal and hexagonal rings) for the VC_{23} , PdC_{23} , RhC_{23} , RuC_{23} , AuC_{23} and MnC_{23} clusters is 1.87 (1.88), 2.01 (2.03), 1.93 (1.99), 1.97 (1.87), 2.03 (2.19) and 1.88 (1.94) Å, respectively. This increase in the distance of the M-C bond after doping is attributed to the large atomic radius of the metal atom (which varies from 1.27 for Mn to 1.44 Å for Au), which is greater than that of the C atom (0.77 Å). The C-M-C bond angle has been strongly reduced, and the obtained value is 99.4, 99.5, 92.3, 89.3, 99.5 and 100.7° for the VC_{23} , PdC_{23} , RhC_{23} , RuC_{23} , AuC_{23} and MnC_{23} clusters, respectively. This great reduction in bond angle was ascribed to the strong interaction between the metal and neighboring carbon atoms. The binding energies (E_b) of C_{24} fullerene was found to be - 6.773 eV, indicating a great chemical stability. The E_b was slightly decreased ($\Delta E_b < 5\%$) after doping with V, Pd, Rh, Ru, Au and Mn atoms, reflecting that the binary clusters formed are also chemically stable. NBO analysis demonstrates that the charges (q_M) carried by the V, Pd, Rh, Ru, Au and Mn atoms in the clusters are + 0.560, + 0.516, + 0.371, + 0.279, + 0.700 and + 0.709 |e| respectively. This sizable charge which was transferred from the metal atom to the neighbor carbon atoms in the doped clusters is due to the large difference in electronegativity between the metal (1.63, 2.20, 2.28, 2.20 and 1.55 for V, Pd, Rh, Ru and Mn, respectively) and the carbon (2.55) atoms, except for the Au atom (2.54), where its value is almost equal to that of the carbon atom. Moreover, this large positive charge on the metal atoms indicates that a strong bond of partial ionic character between the metal and neighboring carbon atoms could be manifested after doping. The charge on the metal in the clusters was also estimated by the B3LYP-D3 level, and the obtained values are close to those found by the PBE-D3 method (see Table 1). To further insights on the electronic and adsorption properties of the metal-doped C_{24} clusters, the MEP isosurfaces for the nanoclusters were computed and the results are shown in Fig. 1. The purpose of this analysis is to predict the most favorable adsorption sites of a molecule as NO_2 over the surface of the MC_{23} nanoclusters. The analysis of the MEP isosurface for each configuration demonstrates that the V, Pd, Rh, Ru, Au and Mn atoms in the nanoclusters are positively charged (blue color), suggesting that the metal atom in the cluster can be viewed as the most favorable adsorption site for a nucleophilic attack in comparison with the rest of atoms of the cluster. So, the active-site nucleophile in the N_2O molecule has a great tendency to adsorb over the V, Pd, Rh, Ru, Au and Mn atoms from its O or N atom. This finding is well compatible with the results obtained through the calculations of the condensed Fukui function (f^+) (not shown). The highest f^+ value is predicted for the V atom in the VC_{23} cluster, indicating a high catalytic activity for this atom (site)

relative to the other metal atoms. The chemical hardness (η) and softness (s) as important parameters reflecting the reactivity of the nanoclusters toward the molecules were also calculated, and the values obtained for each nanocluster are reported in Table 1. The analysis of the values of hardness indicate a great enhancement in the reactivity of the C_{24} nanocage (decrease of η) upon doping with V, Pd, Rh, Ru, Au and Mn atoms. In the other words, the VC_{23} , PdC_{23} , RhC_{23} , RuC_{23} , AuC_{23} and MnC_{23} clusters were found to be more reactive than the pure C_{24} nanocage, thereby their interactions with the N_2O molecule should be very strong in comparison with that of the C_{24} fullerene. The softness values of the clusters were raised upon doping (Table 1), implying an improvement in their reactivity, therefore confirms the results predicted for the chemical hardness. The density of states (DOS) for the pristine and metal-doped C_{24} fullerene was shown in Fig. 1. Using the PBE-D3 level of theory, the calculated energy gaps (E_g) of the C_{24} , VC_{23} , PdC_{23} , RhC_{23} , RuC_{23} , AuC_{23} and MnC_{23} clusters are 1.226, 0.362, 0.842, 0.930, 0.371 and 0.719 eV, respectively. So, the C_{24} fullerene behaves as a semiconductor, and the estimated value (1.226 eV) in our study is consistent with the values reported by other theoretical studies [39, 44]. For comparison, the E_g of the above clusters were also calculated by B3LYP-D3 method, and the values predicted are found to be higher than those calculated by PBE-D3 level (see Table 1). The highest E_g values which are obtained by B3LYP level could be explained by the great contribution of HF (20 %) in this hybrid method. Moreover, when the C_{24} fullerene was doped with V, Pd, Rh, Ru, Au and Mn atoms, its energy gap was strongly reduced and the variation in E_g (ΔE_g) varies from 24.1 (VC_{23}) to 70.5 % (RuC_{23}). This reduction in E_g may be ascribed to the metallic character of the V, Pd, Rh, Ru, Au and Mn atoms which were incorporated in the pure C_{24} fullerene. More precisely, the replacement of a carbon atom in the C_{24} fullerene by a metal atom shifts the energy of the HOMO state towards the less negative values (Table 1), thus leading to a great reduction in its gap energy (E_g). The calculated dipole moment (β_T) after substitution of a C atom of C_{24} by a V, Pd, Rh, Ru, Au or Mn atom was considerably augmented with respect to that of the C_{24} cage ($\beta_T = 0$), and the values estimated are 3.366, 1.688, 3.226, 3.362, 0.693 and 2.784 D for the VC_{23} , PdC_{23} , RhC_{23} , RuC_{23} , AuC_{23} and MnC_{23} , respectively. This increase in β_T was due to the large amount of charge which was transferred from metal to carbon atoms.

Table 1

The binding energy (E_b), energy of HOMO and LUMO states (E_H, E_L), energy gap (E_g), chemical hardness (η), softness (s), dipole moment (β_T) and magnetic moment (μ_T) of the C_{24} and MC_{23} ($M = V, Mn, Ru, Au, Pd$ and Rh) clusters.

Cluster	E_b (eV/atom)	E_H (eV)	E_L (eV)	E_g (eV)	ΔE_g (%)	η (eV)	s (eV ⁻¹)	β_T (Debye)	q_M (e)	μ_T (μ_B)
C_{24}	-6.773	-5.641	-4.415	1.226 (2.529)*	-	0.613	0.816	0.00 (0.00)*	-	0
VC_{23}	-6.613	-4.972	-4.610	0.362 (1.897)	-70.5	0.181	2.762	3.366 (4.715)	+ 0.560 (+ 0.857)*	1
MnC_{23}	-6.559	-5.008	-4.290	0.719 (1.670)	-41.4	0.359	1.393	2.784 (3.095)	+ 0.709 (+ 0.957)	3
RuC_{23}	-6.656	-5.182	-4.252	0.930 (2.170)	-24.1	0.465	1.075	3.362 (3.394)	+ 0.279 (+ 0.279)	0
AuC_{23}	-6.455	-5.052	-4.682	0.371 (1.897)	-69.7	0.185	2.703	0.693 (0.855)	+ 0.700 (+ 0.690)	1
PdC_{23}	-6.545	-5.209	-4.367	0.842 (2.020)	-31.3	0.421	1.188	1.688 (1.485)	+ 0.516 (+ 0.512)	0
RhC_{23}	-6.649	-4.911	-4.062	0.849 (2.229)	-30.8	0.425	1.176	3.226 (3.320)	+ 0.371 (+ 0.390)	1
* The values of E_g , β_T , and q_M for the clusters calculated at the B3LYP-D3 level of theory.										

The magnetic moments (μ_T) of the C_{24} , VC_{23} , PdC_{23} , RhC_{23} , RuC_{23} , AuC_{23} and MnC_{23} clusters were also calculated, and the obtained results show a great enhancement in the magnetic properties of the C_{24} fullerene upon its doping with V, Rh, Au and Mn atoms (see Table 1), except for the RuC_{23} and PdC_{23} clusters, where the magnetic moment remains unchanged, thereby the two clusters are found to be nonmagnetic ($\mu_T = 0$). The highest μ_T value was predicted for the MnC_{23} cluster (3 μ_B). A deep study of the magnetic properties of the clusters indicates that the magnetism in the VC_{23} and MnC_{23} clusters is mainly contributed from the local magnetic moment of 3d orbitals, while for the RhC_{23} and AuC_{23} clusters, the contribution of the 4d and 5d orbitals is little. For example, the contribution of 3d state in the total magnetic moment of VC_{23} cluster is 87 %, while the contribution of 4d state in magnetism for RhC_{23} cluster is only 12 %. The β_T and μ_T of the clusters

were also calculated by B3LYP-D3 level, and the obtained results are almost similar to those obtained by PBE-D3 method (Table 1).

3.2 Adsorption of the N₂O molecule over the C₂₄ nanocage

In order to obtain the most stable configurations of the adsorbed N₂O onto the C₂₄ nanocage, the N₂O molecule was placed above the surface of the C₂₄ fullerene with several positions and different orientations. For further clarification, the N₂O molecule was placed over the surface of the C₂₄ cage by its oxygen (orientation 1) or nitrogen (orientation 2) atom. In addition to two previous orientations, a third complex (orientation 3) has also been tested, in which the N₂O molecule was positioned parallel to the surface of the C₂₄ fullerene. Upon full optimizations, two most stable geometries of the N₂O-C₂₄ complexes, namely A and B, were successfully obtained (see Fig. 2). As shown in Fig. 2, the adsorption of the N₂O molecule over the surface of the C₂₄ nanocage was carried out without dissociation and the values calculated of E_{ads} for the two complexes A ($-2.8 \text{ kcal mol}^{-1}$) and B ($-2.7 \text{ kcal mol}^{-1}$), suggest a weak physical adsorption (physisorption). The distance between the O (N) atom of the N₂O molecule and the surface of the C₂₄ nanocage was found to be 3.14 and 3.29 Å for the A and B states, respectively. These large distances confirms the above finding onto the weak interaction between N₂O and C₂₄ fullerene. NBO analysis displays that the charge transferred from the N₂O molecule to the C₂₄ fullerene during the adsorption process is very small (0.017 and 0.006 |e| for the A and B states, respectively), confirming that the interaction between both species is weak. The above results have also been supported by the calculations of the electron density difference (EDD) isosurfaces for the two complexes (see Fig. 2), which indicate that there is no significant electron density accumulation between the N₂O molecule and the surface of the C₂₄ nanocage, thereby the N₂O molecule is physically adsorbed onto the surface of the C₂₄ fullerene. The density of states (DOS) for the two configurations (A and B) was calculated and the curves obtained are illustrated in Fig. 2. As it was shown in this figure, the energy gap (E_g) of the C₂₄ fullerene after its interaction with the N₂O molecule remain almost unchanged (1.220 and 1.209 eV for the A and B states, respectively), thus the variation in E_g is less than 1.5 %, suggesting that the pure C₂₄ nanocage is an insensitive nanomaterial toward the N₂O molecule. The calculated values of the hardness (softness) demonstrated that the stability of the C₂₄ nanocage has also remained unchanged upon adsorption process. The dipole moments (β_T) of the N₂O-C₂₄ complexes (A and B) were slightly increased after its interaction with the N₂O molecule, and the estimated values are 0.18 and 0.16 D (Table 2) for the configurations A and B, respectively. This little change in the electronic properties of the C₂₄ fullerene was ascribed to low charge transfer between both species. The interaction distance, energy gap, charge transfer, dipole moment and adsorption energy of the complexes (A and B) were also calculated by the B3LYP-D3 method, and the values obtained are consistent with those obtained from the PBE-D3 level of theory.

Table 2

The interaction distance (d), energies of HOMO and LUMO orbitals (E_H, E_L), energy gap (E_g), hardness (η), softness (s), charge transfer (q_T), dipole moment (β_T) and adsorption energy (E_{ads}) for the formed complexes from the interaction between the N_2O molecule and the clusters.

Complex	d (Å)	E_H (eV)	E_L (eV)	E_g (eV)	η (eV)	s (eV ⁻¹)	q_T (e)	β_T (Debye)	E_{ads} kcal.mol ⁻¹
C₂₄⁻ Complex									
A	3.14 (3.10)*	-5.647	-4.426	1.220 (2.527)*	0.610	0.820	+ 0.017 (0.015)*	0.18 (0.06)*	-2.8 (-2.5)*
B	3.29 (3.50)	-5.659	-4.450	1.209 (2.517)	0.605	0.826	+ 0.006 (0.006)	0.16 (0.11)	-2.7 (-2.4)
VC₂₃⁻ Complex									
C	2.18 (2.23)	-4.777	-4.212	0.565 (2.027)	0.283	1.767	+ 0.180 (0.139)	5.51 (7.11)	-15.0 (-14.0)
D	2.03 (2.13)	-4.899	-4.212	0.687 (2.048)	0.344	1.453	+ 0.136 (0.157)	3.88 (6.40)	-24.7 (-18.1)
E	1.60 (1.60)	-5.447	-4.725	0.722 (1.916)	0.361	1.385	-0.059 (-0.152)	2.68 (3.36)	-88.1 (-90.4)
MnC₂₃⁻ Complex									
F	2.31 (2.33)	-4.823	-4.122	0.701 (1.684)	0.351	1.425	+ 0.099 (0.089)	4.826 (5.19)	-9.8 (-10.7)
G	2.07 (2.19)	-4.740	-4.239	0.501 (1.569)	0.251	1.992	+ 0.092 (0.106)	4.86 (5.81)	-15.0 (-12.6)
H	1.59 (1.61)	-5.533	-4.869	0.664 (1.731)	0.332	1.506	-0.228 (-0.409)	2.83 (4.51)	-52.8 (-45.8)
RuC₂₃⁻ Complex									
I	2.50 (2.49)	-5.094	-4.151	0.943 (2.189)	0.471	1.062	+ 0.081 (0.081)	4.34 (4.34)	-8.4 (-9.5)
J	2.18 (2.22)	-5.072	-4.182	0.891 (2.116)	0.445	1.124	+ 0.084 (0.098)	4.38 (4.44)	-13.3 (-11.9)
K	1.75 (1.75)	-5.436	-4.694	0.742 (2.095)	0.371	1.348	-0.147 (-0.234)	2.34 (2.99)	-24.6 (-25.4)

* The values obtained for the clusters by using the B3LYP-D3 level of theory.

Complex	d (Å)	E _H (eV)	E _L (eV)	E _g (eV)	η (eV)	s (eV ⁻¹)	q _T (e)	β _T (Debye)	E _{ads} kcal.mol ⁻¹
PdC ₂₃ ⁻ Complex									
L	2.62 (2.64)	-5.124	-4.267	0.857 (2.050)	0.428	1.168	+0.089 (0.057)	2.816 (2.54)	-6.9 (-7.5)
M	2.31 (2.43)	-5.056	-4.259	0.797 (1.970)	0.399	1.253	+0.098 (0.094)	3.413 (2.93)	-9.3 (-7.8)
P	1.81 (1.80)	-5.893	-5.094	0.799 (1.987)	0.399	1.253	-0.432 (-0.460)	4.959 (5.91)	-2.3 (0.3)
RhC ₂₃ ⁻ Complex									
Q	2.59 (2.60)	-4.826	-3.967	0.860 (2.251)	0.430	1.163	+0.061 (0.058)	4.426 (4.53)	-6.5 (-7.0)
R	2.16 (2.23)	-4.786	-3.952	0.834 (2.205)	0.417	1.199	+0.098 (0.106)	4.680 (4.90)	-12.9 (-10.8)
S	1.87 (1.91)	-5.679	-4.809	0.870 (2.072)	0.435	1.149	-0.157 (-0.211)	2.876 (3.16)	-11.1 (-16.3)
AuC ₂₃ ⁻ Complex									
T	2.70 (2.69)	-5.111	-4.542	0.569 (2.001)	0.285	1.754	+0.062 (0.055)	1.81 (2.05)	-6.8 (-7.9)
W	2.35 (2.37)	-5.069	-4.442	0.627 (2.003)	0.313	1.597	+0.079 (0.081)	2.86 (3.10)	-8.3 (-7.6)
* The values obtained for the clusters by using the B3LYP-D3 level of theory.									

3.3 Adsorption of the N₂O molecule over the VC₂₃ cluster

In order to evaluate the adsorption properties of the metal-doped C₂₄ fullerene, we have studied the interaction of the N₂O molecule with the surface of the VC₂₃ cluster using the PBE-D3 level of theory. For comparison, the B3LYP-D3 method was also employed in our calculations to estimate the stability and electronic properties of the formed complexes between the cluster and the above molecule. Upon optimizations, the results demonstrate that the adsorption of the N₂O molecule over the surface of the VC₂₃ cluster was carried out either associatively or dissociatively (see Fig. 3). When the N₂O molecule has been adsorbed on the VC₂₃ surface through its oxygen atom, the decomposition of the N₂O molecule into O* and N₂ can occurs easily on the vanadium atom of the cluster (configuration E). In this case, the V atom in the cluster is considered as a catalytically active site for this type of the reaction. To better understand the mechanism of the N₂O decomposition on the cluster surface, this reaction will be studied in depth in the Sect. 3.6. The most stable adsorption configurations which were obtained after full optimizations are shown in Fig. 3. The density of

states (DOS) and electron density difference (EDD) isosurfaces of the formed complexes upon the adsorption process were illustrated in the same figure. The electronic properties and reactivity descriptors of these complexes have also been calculated and listed in Table 2. As it was shown in Fig. 3, the distance of the V-C bond has not been changed for the two configurations (C and D) upon the associative adsorption of the N_2O molecule over the cluster surface. While for the configuration E, in which the adsorbed N_2O molecule on the VC_{23} cluster was dissociated to form N_2 molecule and O_{ads} atom, the V-C bond length was strongly modified, and its value was increased from 1.87 and 1.88 Å in the isolated VC_{23} cluster (without interaction with N_2O) to 2.00 and 2.11 Å in the OVC_{23} complex, indicating a great interaction between the VC_{23} cluster and the N_2O molecule with respect to that observed for the C and D complexes. The C-M-C bond angle was reduced from 99.4° in the VC_{23} cluster to 82.0° in the E complex, whereas it remains unchanged for the other two complexes (C and D). In conclusion, the associative adsorption of N_2O over the VC_{23} cluster causes a slight change in their structural parameters, while for the dissociative adsorption of N_2O over the cluster surface provokes a significant modification in their structural parameters, which is due to great interaction between both species. In the other hand, the distance of N-O in N_2O molecule was slightly increased from 1.18 Å in the isolated N_2O molecule to 1.20 Å in the C state, whereas for the D state, the distance of the N-O bond remains almost unchanged (1.17 Å). For the E configuration, the N_2O molecule breaks down into O_{ads} and N_2 molecule, and the dissociated O atom was strongly bonded to the V atom of the cluster, reflecting a strong chemical bond between the two species with a V-O bond length of 1.60 Å. The calculated charges on V (+ 1.254 |e|) and O (- 1.254 |e|) atoms in the complex E indicate that the V-O bond has a greater ionic character. The calculated adsorption energies (E_{ads}) are $-15.0 \text{ kcal mol}^{-1}$ and $-24.7 \text{ kcal mol}^{-1}$ for the C and D states, respectively, suggesting a chemisorption process. Contrariwise to the above configurations, the calculated E_{ads} for the dissociative adsorption of the N_2O molecule over the surface of the VC_{23} cluster ($-88.1 \text{ kcal mol}^{-1}$) was found to be much higher than the obtained values for the C and D configurations, reflecting a strong interaction between both species, which effectively leads to the decomposition of the N_2O molecule into O^* and N_2 molecule. Thereby, the VC_{23} nanocluster could be employed as an efficient nanocatalyst for the decomposition reaction of nitrous oxide.

Based on NBO analysis, the charges of 0.180 and 0.136 |e| are transferred from the adsorbed N_2O molecule to the VC_{23} cluster in the C and D states, respectively. While for the E state, the charge transfer (0.059 |e|) occurs from the cluster to the N_2O molecule. The nature of the bonding between the cluster and the molecule in the formed complexes can be assessed by calculating the electron density difference (EDD) isosurfaces. The results obtained for the complexes C, D and E are plotted in Fig. 3. For the complexes C and D, we observe a large accumulation of electron density between the V atom of the cluster and the O (N) atom of the N_2O molecule which confirms a chemical adsorption (chemisorption) between the N_2O and the VC_{23} surface. Also, after the dissociation of N_2O molecule on the metal site of the cluster, a considerable accumulation of electron density between the carbon of the VC_{23} cluster and the N_2 molecule has been obtained (Fig. 3), indicating a weak chemical adsorption. The distance between the cluster and the N_2 molecule is only 2.13 Å. This molecular chemisorption has also been confirmed by calculating the adsorption energy which was found equal to $-15.4 \text{ kcal mol}^{-1}$. The energy gap, chemical hardness, softness and dipole moment of the complexes formed by the interaction of the VC_{23} cluster with the N_2O molecule were also computed and the values obtained are

summarized in Table 2. The calculations with the PBE-D3 method reveal that the energy gap of the VC₂₃ cluster was largely augmented upon adsorption of N₂O on its surface. For example, the variation in E_g after adsorption process for the configuration D is approximately 90 %. This indicates that the VC₂₃ cluster is very sensitive to the presence of the N₂O molecule on its surface. Using the B3LYP-D3 level of theory, the results exhibit that the E_g was slightly augmented from 1.897 eV for the pure VC₂₃ cluster to 2.027 eV and 2.048 eV for the C and D states, respectively, while for the configuration E, the E_g value remain almost unchanged (1.916 eV). And further to the above, these values are higher than those obtained by the PBE-D3 level, and the increase in E_g for the complexes formed by interaction between the cluster and the N₂O molecule reflects a great stability compared to the VC₂₃ cluster. The hardness (softness) of the VC₂₃ cluster was increased (decreased) upon the N₂O adsorption, implying that the formed complexes after adsorption process are more stable than the VC₂₃ cluster, confirming the above result. Also, the β_T values of the complexes have been augmented from 3.366 Debye (VC₂₃) to 5.510 (configuration C) and 3.880 Debye (configuration D), while for the E configuration, the dipole moment value was hardly reduced (2.680 Debye). This small change in the β_T is due to the little charge transfer between the cluster and the N₂O molecule during the adsorption process. The calculations of the electronic and adsorption properties of the formed complexes which were carried out by the B3LYP-D3 method lead to the same previous conclusions.

3.4 Adsorption of the N₂O molecule over the MnC₂₃ cluster

Before optimization of the MnC₂₃-N₂O complexes, the single N₂O molecule was placed onto the surface of the MnC₂₄ cluster in several orientations in aim to obtain the most stable adsorption configurations. After calculations, three stable configurations of the N₂O-MnC₂₃ complexes, called F, G and H, were predicted, and their optimized geometries with their structural parameters are displayed in Fig. 4. This interaction between the N₂O molecule and the MnC₂₃ cluster has been investigated using the PBE-D3 level of theory. The energies of HOMO and LUMO states, energy gap, chemical hardness, softness, charge on N₂O and dipole moment of the complexes F, G and H are summarized in Table 2. For comparison, the properties of the interactions between the two previous species were also calculated by the B3LYP-D3 level and the obtained results are reported in the parentheses in the same above table. As previously, two types of adsorption were obtained during the interaction of the N₂O molecule over the surface of the MnC₂₃ cluster. The first type is a molecular adsorption (F and G configurations), where the N₂O is associatively adsorbed over the cluster surface, while the second type is a dissociative adsorption (H configuration). For the associative adsorption, the interaction distances between the N₂O molecule and the Mn atom of the MnC₂₃ cluster are found to be 2.07 and 2.31 Å for the configurations G and F, respectively, which are slightly greater than the value obtained for the C and D complexes. This finding indicates that the interaction of the N₂O molecule with the MnC₂₃ cluster is weaker in comparison with that observed between the VC₂₃ and the N₂O molecule in the C and D configurations. Moreover, the Mn-C bond length in the formed complexes was found almost unchanged after the associative adsorption process (Fig. 4). Also, upon interaction of the N₂O with the surface of the MnC₂₃ nanoclusters, the distance of N-N bond in N₂O molecule was hardly reduced from 1.18 Å in the isolated N₂O molecule to 1.12 and 1.13 Å for the F and G states, while the N-O bond length in N₂O has been slightly increased for the two configurations (F and G). For the H configuration, the interaction of the N₂O molecule with the Mn atom of the

cluster leads easily to the dissociation of the molecule into O_{ads} and N_2 species. The new formed bond between the Mn and O atoms in the complex H is equal to 1.59 Å. The electronic and adsorption properties of the MnC_{23} cluster after its adsorption process with the N_2O molecule were calculated and the results reported in Table 2 show that the adsorption energies range from -9.8 (F state) to -52.8 (H state) $kcal\ mol^{-1}$, which are lower than those obtained for the complexes C, D and E. As expected, the dissociative adsorption of the N_2O on the cluster has the highest E_{ads} value compared to the other studied configurations. The obtained values of E_{ads} suggest a weak chemisorption between the N_2O molecule and the MnC_{23} cluster for the F and G states, while for the H configuration, a strong chemisorption between both species was clearly observed, which easily leads to the dissociation of N_2O molecule into O_{ads} and N_2 species. In addition, the E_{ads} value for the H configuration is lower than that obtained for the E complex, indicating that the N_2O decomposition reaction on the VC_{23} cluster was found to be more exothermic than that over the MnC_{23} cluster. This reflects that the N_2O decomposition reaction could proceed on the surface of the MnC_{23} cluster more easily than that over the VC_{23} cluster. Therefore, the MnC_{23} nanocluster could also be employed as a promising nanocatalyst for the dissociation of N_2O into O^* and N_2 molecule. In this case, the Mn atom plays a major role in the above reaction, where it acts as an active surface site to facilitate the adsorption and dissociation of the N_2O molecule. So, it has a great intrinsic catalytic activity compared to that of the rest of the atoms of the cluster.

Based on the density of state (DOS), the calculated energy gaps are 0.701, 0.501 and 0.664 eV for the F, G and H complexes, respectively. Compared to the E_g of the MnC_{23} cluster (0.719 eV), the variations in energy gap (ΔE_g) are 2.5 and 7.6 % for the F and H states, respectively, indicating a lower electronic sensitivity of the MnC_{23} nanocluster toward the presence of the N_2O molecule onto its surface, while for the G configuration, where the adsorption onto the cluster surface was carried out by its nitrogen atom, the ΔE_g is 30.3 %, implying a great electronic sensitivity of this cluster to the N_2O molecule. The ΔE_g of all studied complexes which are calculated by B3LYP-D3 level (see Table 2) was found to be less than 5 %, implying that the MnC_{23} nanocluster is insensitive to the N_2O molecule. This result indicates that the MnC_{23} nanocluster is not an appropriate nonmaterial for the detection of the N_2O molecule, but its great reactivity in the N_2O decomposition reaction make it an efficient nanocatalyst for this type of the reaction. NBO analysis indicates that the amounts of charge transferred from the N_2O molecule to the MnC_{23} cluster are 0.099 and 0.092 |e| for the configurations F and G, respectively. While, for the H configuration, where the N_2O molecule was dissociatively adsorbed over the MnC_{23} cluster, a considerable charge of 0.228 |e| was transferred from the cluster to the molecule. The EDD isosurface of the complex G shows a substantial electron density accumulation around the V-N bond which is the result of a strong chemical adsorption between both species. In contrast to configuration G, a little accumulation of electron density between the O atom of the N_2O and the V atom of the cluster was observed for the F configuration, indicating a weak chemisorption. The dissociative adsorption of the N_2O over the surface of the MnC_{23} cluster (H state) leads to a new $OMnC_{23}$ complex and a free N_2 molecule, and the calculated E_{ads} for the interaction between the $MnC_{23}O$ cluster and the N_2 molecule suggests a weak physical adsorption ($E_{ads} = -3.8\ kcal\ mol^{-1}$). This finding was confirmed by the absence of the accumulation of electron density between the formed $OMnC_{23}$ cluster and the N_2 molecule (Fig. 4). The hardness (softness) of the MnC_{23} cluster was hardly reduced (increased) after adsorption process (Table 2), and the values predicted by PBE-D3 level are in the range of 0.251 (1.992) to 0.351 (1.425 eV^{-1}) eV, indicating that the reactivity of the

clusters was slightly improved upon its interaction with the N_2O molecule. As an example, when the N_2O molecule was interacted with the surface of the MnC_{23} cluster in H complex, its hardness was diminished of 7.5 %. This result can be ascribed to low charge transfer between both species during the complexation process. The results show also that the dipole moment (β_T) of the MnC_{23} cluster (2.784 D) has been slightly augmented upon its complexation with the N_2O molecule, and the calculated values are 4.826, 4.860 and 2.830 D for the F, G and H complexes, respectively. Furthermore, in comparison with the results obtained by the PBE-D3 functional, the calculations of the properties of the complexes carried out by the B3LYP-D3 level leads to the same previous conclusions (see Table 2).

3.5 Adsorption of the N_2O molecule over the Ru-, Pd-, Au- and Rh-doped C_{24} clusters

In this section, we examined the adsorption of the N_2O molecule over the surface of the Ru-, Pd-, Au- and Rh-doped C_{24} clusters in the same manner as above. Upon optimizations, three most stable adsorption configurations for each complex were identified with the exception of the AuC_{23} cluster, whose interaction with the N_2O molecule only leads to two stable complexes. In this case, the decomposition of the N_2O molecule will not occur over the surface of the AuC_{23} cluster, probably due to large activation energy (E_a) required by the N_2O dissociation reaction onto the metal site of the cluster. All the optimized geometries of the complexes and their structural parameters were shown in Figures S1-S4 (Supplementary Information). The energies of HOMO and LUMO states, energy gap, hardness, softness, charge transfer and dipole moment of the complexes have also been calculated and listed in Table 2. The interaction strength between the cluster and the N_2O molecule was evaluated by calculating the adsorption energy (E_{ads}), and the obtained values are reported in the above table. For the configurations I, L, Q and T, the N_2O molecule was weakly physisorbed over the Ru, Pd, Rh and Au atoms of the clusters by its oxygen atom with adsorption energies of -8.4 , -6.9 , -6.5 and $-6.8 \text{ kcal mol}^{-1}$, respectively. The interaction distances between the metal atom of the clusters and the O atom of the N_2O molecule are found to be 2.50, 2.62, 2.59 and 2.70 Å for the I, L, Q and T states respectively. The interaction of the N_2O molecule with the RuC_{23} and RhC_{23} clusters from its nitrogen atom (J and R states) was identified as a weak chemisorption with adsorption energies of -13.3 and $-12.9 \text{ kcal mol}^{-1}$, respectively. On the contrary, the adsorption of N_2O over the PdC_{23} and AuC_{23} clusters by its nitrogen atom is viewed as a physical adsorption (physisorption) with adsorption energies which vary from -9.3 (M state) to -8.3 (W state) kcal mol^{-1} . The calculated lengths of the M-N bond in the $\text{NO}_2\text{-RuC}_{23}$ and $\text{NO}_2\text{-RhC}_{23}$ complexes are 2.18 and 2.16, respectively, which are lower than those obtained for the $\text{NO}_2\text{-PdC}_{23}$ (2.31 Å) and $\text{NO}_2\text{-AuC}_{23}$ (2.35 Å) complexes, confirming that the interaction between the N_2O molecule and the metal site in the J and R configurations is higher than that obtained in the M and W complexes. This finding suggests that the interaction of the N_2O molecule with the surface of the cluster through its nitrogen atom is stronger than that by its oxygen atom. This was confirmed by the highest values of the adsorption energies which were obtained for the formed complexes through the N_2O adsorption over the metal atom of the clusters by its nitrogen atom with respect to those formed by the interaction of N_2O with the clusters by its oxygen atom. Moreover, the results reveal that the adsorption energy increases with the decrease of the interaction distance between the cluster and the N_2O molecule. In other words, the shorter the bond length between the cluster and the N_2O

molecule, the greater the adsorption energy. The results indicate also that the interaction of the N_2O with the surface of the RuC_{23} , PdC_{23} , RhC_{23} and AuC_{23} clusters is less greater than that observed for the VC_{23} and MnC_{23} clusters, demonstrating a low reactivity of the former clusters toward the N_2O molecule compared to the latter ones. The configurations K, P and S were identified as a decomposition reaction of the N_2O molecule onto the surface of the RuC_{23} , PdC_{23} and RhC_{23} cluster, respectively, in which the N_2O molecule was dissociated over the metal site to form O^* and N_2 species. The calculated adsorption energies are -24.6 , -2.3 and $-11.1 \text{ kcal mol}^{-1}$ for the K, P and S complexes, respectively. Upon the dissociative process, the distances of the M-O bond in the OMC_{23} clusters are found to be 1.75, 1.81 and 1.87 Å for the K, P and S states, respectively. NBO analysis reveals large charges on the metal atoms after the formation of the complexes, reflecting the creation of a great chemical bond with ionic character between the metal and oxygen atoms. The results show also that the length of the M-C bond (C-M-C angle bonds) of the complexes which is shared between square-hexagonal rings was slightly increased (decreased) after their interaction with the N_2O molecule. It should also be mentioned that the calculations proved that the dissociation of the N_2O molecule over the metal site of the AuC_{23} cluster was not possible due to the large activation energy required by the N_2O decomposition reaction. An identical result was observed for the AuC_{19} cluster, in which only associative adsorption was obtained when the N_2O molecule was interacted with the surface of the cluster [45]. NBO analysis also indicates that the charge transfer during the complexation process was carried out from the N_2O to the clusters for the molecular adsorption, while for the dissociative adsorption, the charge has been transferred from the clusters to the N_2O molecule. Furthermore, the amounts of charge transferred between both species during the dissociative adsorption are greater than those estimated for the molecular adsorption, implying that the dissociative adsorption of the N_2O molecule over these clusters was found to be more favorable than the molecular adsorption. Using the B3LYP-D3 level, the results show that the quantity of charge transferred between the N_2O molecule and the clusters during the complexation process is very close to that calculated by the PBE-D3 method (see Table 2). In order to evaluate the different types of interactions existing in the complexes formed during the adsorption process, the electron density difference (EDD) isosurfaces for each configuration were calculated and reported in Figures S1-S4. As one can see from this figure, for the J and R complexes, where the interaction between both species is considered as a weak chemical adsorption, the accumulation of the electron density was found strongly localized between the surface of the cluster and the N_2O molecule. While for the I, L, M, Q, T and W complexes, where the N_2O molecule was physisorbed over the metal atom of the clusters, a low electron density accumulation was observed between the metal atom of the clusters and the N_2O molecule. For the dissociative adsorption of N_2O , an appreciable accumulation of the electron density between the formed OMC_{23} clusters and the N_2 molecule was noticed in R state (Figure S3), suggesting a chemical adsorption, while for the P and K configurations, where the electron density accumulation between both species was found to be negligible (Figures S1-S2), the interaction between both species is considered as a weak physical adsorption. These results are supported by the calculated values of E_{ads} of the adsorbed N_2 on the surfaces of the OMC_{23} clusters. For the K and P configurations, the adsorption energies are -7.5 and $-3.5 \text{ kcal mol}^{-1}$, respectively, while for the R configuration, the calculated value of E_{ads} is $-11.3 \text{ kcal mol}^{-1}$, which is much greater than those obtained for the above complexes.

The energy gap of the PdC_{23} , RuC_{23} and RhC_{23} clusters was slightly changed after their interaction with the N_2O molecule. While for the AuC_{23} cluster, its E_g was largely increased upon adsorption process, and the calculated ΔE_g was found to be 53.4 and 69.0 % for the complexes T and W respectively. These results indicate that the stability of all studied clusters remains almost unchanged after their complexation with the N_2O molecule, except for the AuC_{23} cluster, where its stability was largely increased after adsorption process. In conclusion, when the N_2O is adsorbed over the surface of the clusters, their energy gaps are not affected, except for the AuC_{23} cluster, where its E_g was greatly augmented. The values of hardness (softness) of the clusters has also been slightly changed upon adsorption process (except for the AuC_{23} cluster where its η (s) was augmented (decreased)). This indicates that the reactivity of these clusters remains invariant (except for the AuC_{23} cluster, where its reactivity was greatly increased), confirming the above results obtained for the energy gaps. Unlike the gap energy, the dipole moments of the clusters are strongly influenced by the adsorption process and the calculated values for the complexes were increased from 1.810 (complex T) to 4.959 D (complex P). The electronic and adsorption properties and reactivity descriptors (E_g , η , s , β_T and E_{ads}) of the formed complexes have also been computed by the B3LYP-D3 method, and the results obtained fit well with those predicted by the PBE-D3 level of theory, except for the energy gaps of the complexes, in which the estimated values are found to be greater than those calculated by the PBE-D3 level (see Table 2). This large difference in E_g was explained by the great contribution of Hartree-Fock exchange-energy (20 %) in the hybrid-B3LYP functional which tends to stabilise the HOMO state [46].

3.6 Catalytic performances of the MC_{23} clusters in the N_2O dissociation reaction

To further study the catalytic performances of the VC_{23} , MnC_{23} , RhC_{23} , RuC_{23} and PdC_{23} clusters which were identified as efficient nanocatalysts capable to dissociates the N_2O molecule into N_2 and O_{ads} species, we have studied the mechanism of the N_2O decomposition by determining the transition state structures which can manifest between the reactants and products. As it was mentioned in previous sections, the adsorption energy of the N_2O molecule onto the clusters from its oxygen is lower than that of its nitrogen atom, indicating that the interaction between the cluster and the oxygen atom of the N_2O molecule is weak, thereby it does not require a large activation energy to start the N_2O decomposition reaction. In catalysis, a nanomaterial is considered to be an active and efficient nanocatalyst in a chemical reaction if it has a low activation energy. Therefore, the lower the activation energy, the higher the catalytic activity of the nanocatalyst in the chemical reaction. Based on the optimized configurations of the reactants and TS and their total energies, the activation energies of the N_2O decomposition reaction for all studied clusters were calculated. The structures of the reactants, transition states and products of the five clusters are shown in Fig. 5 and the calculated values of the activation energies (E_{ac}) and the reaction energies (E_r) for each studied cluster are listed in Table 3. The reaction energy for the N_2O dissociation in the presence of the clusters are in the range of -0.9 to $-76.9 \text{ kcal mol}^{-1}$, implying an exothermic process. The obtained results show that the activation energies of the N_2O decomposition in the presence of the VC_{23} and MnC_{23} clusters are found to be lower in comparison with those obtained for the other clusters (Table 5), indicating that the two clusters could be viewed as very active and efficient nanocatalysts for the N_2O dissociation reaction. The values of the barrier energies for the VC_{23} and

MnC₂₃ clusters are estimated to be 9.3 and 7.9 kcal mol⁻¹, respectively. In comparison these values with the calculated E_{ac} for the other clusters which were employed as nanocatalysts in the N₂O dissociation such as magnesium oxide (32 kcal mol⁻¹), manganese-embedded graphene (74 kcal mol⁻¹) and selenium-doped graphene (41 kcal mol⁻¹), the VC₂₃ and MnC₂₃ clusters are found to be more active and efficient nanocatalysts in the N₂O decomposition reaction compared to the catalysts listed above [47–49]. The result indicates also that the MnC₂₃ cluster is more active than the VC₂₃ cluster. Other theoretical studies show that the calculated values of E_{ac} for the N₂O dissociation in the presence of the Fe- and Si-embedded graphene are 8 and 12 kcal mol⁻¹, respectively, which are comparable to our results [50–51]. As the catalytic activity of the nanocatalysts is essentially related to the step of the N₂O dissociation into N₂ and O* (N₂O → N₂ + O*), which was considered as the rate-determining step of the N₂O decomposition reaction, we have compared the catalytic performances of the clusters and the results demonstrates that the VC₂₃ and MnC₂₃ possesses a high catalytic activity with respect to that obtained for the other clusters (Ru-, Rh- and PdC₂₃). Also, their reactivity was found to be much higher compared to that of the nanocatalysts reported in the literature for the same reaction. Therefore, the VC₂₃ and MnC₂₃ clusters could be employed as effective nanocatalysts for the adsorption and dissociation of the N₂O molecule at low temperatures. In addition to above, the important results obtained in this study may point direct researchers to new perspectives for further studies on the fullerene-based nanocatalysts that exhibit high catalytic activity in the N₂O dissociation reaction at lower temperatures.

Table 3
The activation energy and reaction energy for the N₂O decomposition reaction in the presence of the MC₂₃ (M = V, Mn, Ru, Pd and Rh) clusters.

Cluster	Activation energy (kcal mol ⁻¹)	Reaction energy (kcal mol ⁻¹)
VC ₂₃	9.3	- 76.9
MnC ₂₃	7.9	- 49.9
RuC ₂₃	24.4	- 24.6
PdC ₂₃	33.5	- 0.9
RhC ₂₃	42.4	- 11.7

4. Conclusions

The stability and electronic properties of the C₂₄ and MC₂₃ (M = V, Mn, Ru, Pd, Rh and Au) clusters and their interactions with the N₂O molecule were investigated using DFT calculations at the PBE-D3 level of theory. For comparison, the electronic and adsorption properties of the above clusters have also been evaluated by using the B3LYP-D3 method. When a carbon atom of the C₂₄ fullerene was replaced by a transition metal atom, the reactivity of the C₂₄ was significantly enhanced, and the metal atom in the nanoclusters can be considered as

the most favorable adsorption site for the rich-electrons molecules. The results show that the N_2O adsorption over the surface of the MC_{23} clusters can be carried out either associatively or dissociatively (except for the AuC_{23} cluster). For the dissociative adsorption, the N_2O molecule break down on the metal site of the cluster to form O^* and N_2 species. In this case, the oxygen atom released by the N_2O molecule has been strongly chemisorbed on the metal atom of the cluster by forming a chemical bond of ionic character. In the case of the molecular adsorption, the interaction between the surface of the C_{24} fullerene and the N_2O molecule was considered as a weak physical adsorption. For the MC_{23} clusters, the N_2O molecule was greatly adsorbed over their surface by its nitrogen atom with adsorption energies which vary from -12.9 (R state) to -24.7 (D state) kcal mol^{-1} , indicating a chemisorption process. While, the adsorption of the molecule on the MC_{23} clusters from its oxygen atom was regarded as a physical adsorption with E_{ads} less than $-10 \text{ kcal mol}^{-1}$. So, the interaction of the N_2O with the surface of the clusters via its oxygen atom was found lower than that by its nitrogen atom. Moreover, the calculated E_{ads} of the N_2O on the VC_{23} and MnC_{23} clusters are found higher than those predicted for the other clusters, reflecting a strong interaction between the N_2O molecule and the VC_{23} and MnC_{23} clusters with respect to that observed for the other clusters. Contrariwise to the associative adsorption, the N_2O molecule can be dissociatively adsorbed over the surface of the MC_{23} clusters, in which the N_2O molecule decomposes on the metal site of the clusters to form O_{ads} and N_2 species. The calculated adsorption energies are -88.1 , -52.8 , -24.6 , -2.3 and $-11.1 \text{ kcal mol}^{-1}$ for the configurations E, H, K, P and S, respectively. Therefore, these nanoclusters could be used as efficient nanocatalysts for the decomposition of N_2O molecule. A more in-depth study on the mechanism of the N_2O dissociation reaction which take place over the metal atom of the clusters shows that the values of the activation energies which were calculated from the difference between the total energies of the reactants and the transition states are in the range of -7.9 to $-42.4 \text{ kcal mol}^{-1}$. The values of the reaction energies are found to be negative and the calculated E_{R} vary from -0.9 to $-76.9 \text{ kcal mol}^{-1}$, reflecting that the reaction is an exothermic process. Furthermore, the analysis of the mechanism of the N_2O dissociation reaction onto different studied clusters indicate that the lowest barrier energies (E_{ac}) were obtained for the VC_{23} ($9.3 \text{ kcal mol}^{-1}$) and MnC_{23} ($7.9 \text{ kcal mol}^{-1}$) clusters in comparison with the other clusters, implying that the catalytic activity of the VC_{23} and MnC_{23} clusters as nanocatalysts in the N_2O dissociation reaction is much higher than that of the PdC_{23} , RuC_{23} and RhC_{23} clusters. Moreover, the dissociation of the N_2O into O^* and N_2 over the surface of the MnC_{23} nanocluster occurs more easily than on the VC_{23} cluster. This finding indicates that the reactivity of the MnC_{23} clusters in the above reaction is greater than that obtained for the VC_{23} cluster. Also, the values of E_{ac} for the VC_{23} and MnC_{23} clusters are found to be lower than those obtained for the Mn-, Se- and Si-embedded graphene and magnesium oxide, demonstrating that the latter nanocatalysts are found to be less effective than the VC_{23} and MnC_{23} clusters in the N_2O dissociation reaction. This indicates that the VC_{23} and MnC_{23} clusters could be employed as active and efficient nanocatalysts for the decomposition of N_2O molecule.

These important results obtained in this study on the fullerene-based clusters used as nanocatalysts for the N_2O decomposition reaction could prompt researches to continue their studies on the development of this type of nanomaterial and to investigate other types of fullerenes to evaluate their reactivity in various chemical reactions, including the N_2O dissociation reaction.

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Figures

Figure 1

The optimized configurations, molecular electrostatic potential (MEP) isosurfaces and density of states (DOS) of the C₂₄ and MC₂₃ (M=V, Mn, Au, Rh, Pd and Ru) clusters.

Figure 2

The most stable adsorption configurations, electron density difference (EDD) isosurfaces and density of states for the complexes formed between the C₂₄ cluster and the N₂O molecule (A and B states). The blue and pink colors indicate the electron density loss and gain regions, respectively.

Figure 3

The most stable adsorption configurations, electron density difference (EDD) isosurfaces and density of states for the complexes formed between the VC24 cluster and the N₂O molecule (C, D and E states).

Figure 4

The most stable adsorption configurations, electron density difference (EDD) isosurfaces and density of states for the complexes formed between the MnC₂₄ cluster and the N₂O molecule (F, G and H states).

Figure 5

Potential energy diagrams for the N₂O decomposition ($\text{N}_2\text{O} \rightarrow \text{O}^* + \text{N}_2$) over the MC₂₃ (M = V, Mn, Pd, Rh and Ru) cluster calculated by the PBE level of theory.

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