

# Molecular adsorption of NO on free-standing and on graphene-supported Mo<sub>3</sub>W<sub>5</sub> cluster: a density functional theory investigation

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**Abstract** The adsorption of molecular NO on the free-standing and graphene-supported Mo<sub>3</sub>W<sub>5</sub> cluster is studied using methods from the gradient-corrected density functional theory. Before, the effect of the graphene support on the properties of the metal cluster was investigated. The interaction between the metal cluster and the graphene sheet takes place mainly through W atoms, which form up to three bonds with the support. Interaction energies are in the range from 0.6 to 1.5 eV. An amount of charge of about 0.4–0.5 e<sup>-</sup> is transferred from the cluster to the support. Geometric distortions in the metal aggregate are negligible. An important decrease in the magnetic moment of Mo<sub>3</sub>W<sub>5</sub> with respect to its free-standing value is observed after the interaction with the support. Molecular NO adsorbs on sites involving W atoms only, both for the free-standing and the supported metal cluster. Adsorption energies are in a range from 2 to 4 eV. A parallel mode is the preferred mode from an energetic point of view. Moreover, for that parallel adsorption mode, the N–O bond is more effectively

activated. Magnetic moments change largely after adsorption indicating important rearrangement in the electronic configuration of the metal cluster. An important amount of electronic charge is transferred both from the free-standing and from the supported metal cluster to NO. The amount of charge transferred seems to be closely related to the activation of the N–O bond. The effect of the graphene sheet on the catalytic properties of Mo<sub>3</sub>W<sub>5</sub> seems to be negligible, with the exception of some changes in the electronic configuration of the cluster.

**Keywords** Density functional theory · MoW clusters · Graphene support · Nitric oxide · Modeling and simulation

## Introduction

In a very recent work, the properties of free-standing bimetallic clusters containing Mo and W atoms were studied using tools from the density functional theory (Pis-Diez and Aguilera-Granja 2013). The aim of that contribution was to shed light into the potential catalytic activity of MoW-based aggregates, which could be thought of as catalyst models for hydrotreating (HDT) processes in the petroleum industry (Topsøe et al. 1996). Those systems are unique catalysts for the removal of heteroatoms (N, S) from aromatic compounds present in petroleum streams. In

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the HDT process, the heteroatoms are converted to  $\text{H}_2\text{S}$  and  $\text{NH}_3$ , thus avoiding the strong contaminants  $\text{SO}_2$  and  $\text{NO}_x$ . According to several energetic, geometrical, and electronic criteria, it was concluded in the work mentioned above that the  $\text{Mo}_3\text{W}_5$  aggregate should be a good candidate to take part in a charge transfer reaction.

On the other hand, there has been an increasing interest in graphene as a catalyst and as a catalyst support in heterogeneous catalysis in the past several years (Kong et al. 2014; Fan et al. 2015; Julkapli and Bagheri 2015). For supported metal-based catalysts in particular, it is expected that the chemical bonding and the charge transfer at the interface between the metal particles and support play an important role to achieve higher catalytic activity and selectivity. As an example, the charge transfer between graphene and Au aggregates supported on the carbon catalyst contributes to a significant reduction in the reaction barrier for CO oxidation (Zhou et al. 2010). Charge transfer between graphene and other metals, such as Pt and Cr, was not observed, though (Kim et al. 2012; Wang et al. 2013). Mechanical strain and structural defects have been also proposed to strengthen and even to tailor the interaction between the catalyst and graphene (Fan et al. 2015).

It is also a well-known fact that nitric oxide is a useful spectroscopic probe for investigating active sites on transition metal systems (Kazusaka and Howe 1980). The effect of the particle size on the catalytic properties of Pd catalysts supported on  $\text{SiO}_2$  was investigated utilizing the decomposition of chemisorbed NO and reactions of NO with CO (Xu and Goodman 1994a; Xu et al. 1994b). The reaction of both NO and CO on Cu nanoparticles supported on  $\text{Al}_2\text{O}_3$  was also studied using high-resolution electron energy-loss spectroscopy (HREELS) and temperature-programmed desorption (TPD) (Wu and Goodman 1994). The interaction of NO with  $\text{Rh}_n^\pm$  clusters with up to 30 atoms was studied experimentally by means of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry as a model for the reduction of nitrogen oxides  $\text{NO}_x$  in automobile catalytic converters (Brown and King 2000; Ford et al. 2005; Anderson et al. 2006). Moreover, some theoretical studies were carried out on the reaction of NO with isomers of  $\text{Rh}_6^+$  to support the experimental findings (Harding et al. 2006; Torres et al. 2011).

In the present work, the reaction of the free-standing  $\text{Mo}_3\text{W}_5$  aggregate with NO, used as a probe molecule, is studied from a theoretical point of view to achieve a better understanding of the potential catalytic activity of the bimetallic nanosystem. Moreover, both the structural and electronic effects of graphene as a support on the reaction of  $\text{Mo}_3\text{W}_5$  with NO are also investigated. Tools derived from the density functional theory are used in all cases. The rest of the work is organized as follows. Computational details and models used throughout are presented in Sect. 2. Results on the influence of the graphene support on the properties of isolated  $\text{Mo}_3\text{W}_5$  are reported in Sect. 3. Section 4 is devoted to show the results of the molecular adsorption of NO on both free-standing and supported  $\text{Mo}_3\text{W}_5$ . Finally, main conclusions are summarized in Sect. 5.

### Computational details

Present calculations are based on the density functional theory (DFT) (Parr and Yang 1989) within the generalized gradient approximation (GGA) formulated by (Perdew et al. 1996) as implemented in the computational package Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) (Soler et al. 2002). SIESTA employs a numerical pseudo-atomic orbitals as basis sets to solve the single-particle Kohn–Sham equations, while the atomic cores are described by nonlocal, norm-conserving Troullier–Martins pseudopotentials (Troullier and Martins 1991) factorized in the Kleinman–Bylander form (Kleinman and Bylander 1982).

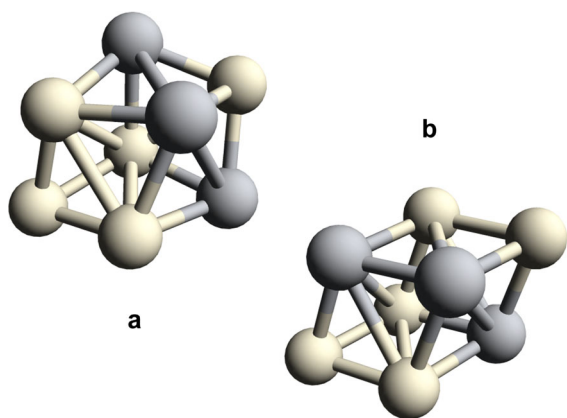
The pseudopotentials for Mo, W, C, N, and O were generated using the  $4d^5 5s^1 5p^0$ ,  $5d^4 6s^2 6p^0$ ,  $2s^2 2p^2$ ,  $2s^2 2p^3$  and  $2s^2 2p^4$  valence configurations, respectively. For Mo and W, the cutoff radii for the d, s, and p states were 1.67 a.u., 2.30 a.u., and 2.46 a.u., and 2.24 a.u., 2.85 a.u., and 3.03 a.u., respectively. For C, N, and O, the cutoff radii for the s, p, and d states were 1.49 a.u., 1.50 a.u., and 2.19 a.u.; 1.24 a.u., 1.24 a.u., and 1.24 a.u.; and 1.14 a.u., 1.14 a.u., and 1.14 a.u., respectively. The valence states were described using a double- $\zeta$  basis set augmented with two polarization functions.

The calculation details concerning the free-standing  $\text{Mo}_3\text{W}_5$  cluster, as well as some simple tests to validate

the methodology and the pseudopotentials, can be found elsewhere (Pis-Diez and Aguilera-Granja 2013).

All the calculations for the graphene-supported  $\text{Mo}_3\text{W}_5$  cluster were performed using a periodic supercell. A rectangular array of  $6 \times 10$  C atoms was used to model the 2D graphene sheet ( $a = 12.96$ ,  $b = 12.47$  Å). The  $\text{Mo}_3\text{W}_5$  cluster was initially located at different sites of the graphene sheet, including on-top, bridge, and hollow sites. The dimension perpendicular to the graphene sheet was set to 16 Å to avoid the interaction of the metallic cluster with neighbor cells.

The putative ground state found for the  $\text{Mo}_3\text{W}_5$  cluster adopts a capped decahedral (CD) structure (Pis-Diez and Aguilera-Granja 2013). A closest isomer is found at only 0.02 eV/at above the ground state. That isomer adopts the structure of a parallelepiped (PL), a more symmetric structure than the CD one mentioned above, see Fig. 1. Due to the low symmetry of the CD structure, the number of starting geometries to study the interaction of the  $\text{Mo}_3\text{W}_5$  cluster with the graphene sheet becomes a huge number. On the other hand, the number of starting geometries reduces considerably if the symmetry of the PL isomer is exploited instead. Moreover, some preliminary tests show that the difference in energies is lower than 0.03 eV/at for the adsorption of NO on selected sites of both free and supported CD and PL aggregates. Those results seem to indicate that the interaction patterns are very similar for both structures. Thus, the PL structure of  $\text{Mo}_3\text{W}_5$  is used throughout the work.



**Fig. 1** Capped decahedral (CD) isomer **a** and parallelepiped (PL) isomer **b** of  $\text{Mo}_3\text{W}_5$ . The PL isomer is only 0.02 eV/at above the CD isomer in atomization energy. Gray and white circles represent Mo and W atoms, respectively

The interaction of the PL structure of  $\text{Mo}_3\text{W}_5$  with the graphene sheet is characterized by the interaction energy:

$$E_{\text{int}} = E_{\text{graphene}} + E_{\text{Mo}_3\text{W}_5} - E_{\text{Mo}_3\text{W}_5/\text{graphene}}, \quad (1)$$

where  $E_{\text{graphene}}$  is the electronic energy of the pristine graphene sheet,  $E_{\text{Mo}_3\text{W}_5}$  is the electronic energy of the free-standing bimetallic cluster in the PL structure, and  $E_{\text{Mo}_3\text{W}_5/\text{graphene}}$  is the electronic energy of the system after interaction.

As a further validation of the methodology, atomization energies and equilibrium distances for  $\text{N}_2$ ,  $\text{O}_2$ , and NO are calculated. Calculated atomization energies are 10.41, 5.04, and 6.54 eV for  $\text{N}_2$ ,  $\text{O}_2$ , and NO, respectively. Those values agree reasonably well with the values of 9.75, 5.11, and 6.60 eV obtained with the coupled cluster method including up to quintuple excitations (Fogueri et al. 2013). Calculated equilibrium distances are 1.12, 1.35, and 1.21 Å for  $\text{N}_2$ ,  $\text{O}_2$ , and NO, respectively. They compare fairly well with the experimental values of 1.098, 1.208, and 1.154 Å (Huber and Herzberg 1979). The previous agreement provides confidence in the computational methodology used in this work.

For the adsorption of NO on the free-standing and the supported  $\text{Mo}_3\text{W}_5$  cluster different sites involving Mo atoms only, W atoms only or both metallic atoms were considered. In those cases, the interaction is characterized by the adsorption energies

$$E_{\text{ads}}^{\text{free}} = E_{\text{Mo}_3\text{W}_5} + E_{\text{NO}} - E_{\text{NO}/\text{Mo}_3\text{W}_5} \quad (2)$$

and

$$E_{\text{ads}}^{\text{supp}} = E_{\text{Mo}_3\text{W}_5/\text{graphene}} + E_{\text{NO}} - E_{\text{NO}/\text{Mo}_3\text{W}_5/\text{graphene}}, \quad (3)$$

where  $E_{\text{NO}}$  is the electronic energy of the NO molecule in its ground state and  $E_{\text{NO}/\text{Mo}_3\text{W}_5}$  and  $E_{\text{NO}/\text{Mo}_3\text{W}_5/\text{graphene}}$  are the electronic energies of the systems after adsorption. The remaining terms were defined after Eq. 1.

All structures were fully optimized using the conjugate gradient method until the interatomic forces were smaller than 0.006 eV/Å. No symmetry or spin constraints were imposed during the optimizations. Only the  $\Gamma$ -point was used for the Brillouin zone integration. An energy cutoff of 250 Ry was adopted to represent the electron density in the real-space grid.

The amount of charge transferred from the bimetallic cluster both to the graphene sheet and to the NO molecule is calculated by subtracting Mulliken charges (Mulliken 1955). The total charge of  $\text{Mo}_3\text{W}_5$  is calculated as the sum of the atomic charges of the 8 atoms,  $Q(\text{Mo}_3\text{W}_5) = \sum_i^3 Q(\text{Mo}_i) + \sum_j^5 Q(\text{W}_j)$ . Then the amount of charge transferred from the isolated cluster to the graphene sheet is obtained as  $\Delta Q = Q^{\text{after}}(\text{Mo}_3\text{W}_5) - Q^{\text{before}}(\text{Mo}_3\text{W}_5)$ , where  $Q^{\text{after}}(\text{Mo}_3\text{W}_5)$  is the total charge of the bimetallic cluster after the interaction and  $Q^{\text{before}}(\text{Mo}_3\text{W}_5)$  is the total charge before the interaction. The charge transferred from supported  $\text{Mo}_3\text{W}_5$  to NO, on the other hand, is obtained from the change in NO Mulliken charges,  $\Delta Q = Q^{\text{after}}(\text{NO}) - Q^{\text{before}}(\text{NO})$ .

### The $\text{Mo}_3\text{W}_5$ cluster supported on a graphene sheet

The most stable conformations of  $\text{Mo}_3\text{W}_5$  supported on a graphene surface are shown in Figs. 2 and 3, whereas selected electronic and geometrical properties of those conformations are presented in Table 1. It can be seen from the table that interaction energies range from about 0.6 to 1.5 eV. The most stable conformations, (a) to (d), are characterized by a bonding pattern in which two metal atoms bind to bridge-like sites involving two carbon atoms. Other conformations also involving two metal atoms, (g) to (i), present different bonding patterns, namely, one metal atom binds to an on-top site and the other metal atom binds either to a bridge site or to a triangular site. However, conformations (g) to (i) are much less favored from an energetic point of view than conformations (a) to (d). Conformations (e) and (f) are characterized by three metal atoms binding both to bridge sites and to triangular sites. Their interaction energies are about 0.4 eV smaller than the values exhibited by conformations (a) to (d). Interestingly, those conformations in which the number of bonds between the metal cluster and the graphene sheet is maximized, that is, (j) and (k), present the lowest interaction energies.

It is shown in Table 1 that the geometrical distortions induced both in  $\text{Mo}_3\text{W}_5$  and in graphene after the interaction are almost negligible. They range from 0.009 to 0.019 Å in the case of the metal cluster and from 0.008 to 0.011 Å in the case of the graphene sheet. Furthermore, no metal-metal bonds are broken

after interaction. Also, metal-carbon distances are in the range from about 2.40 to 2.60 Å, which are considerably larger than the values of 1.753 and 1.777 Å calculated for the MoC and WC diatomic molecules. Those findings seem to suggest that the interaction between  $\text{Mo}_3\text{W}_5$  and graphene is weak.

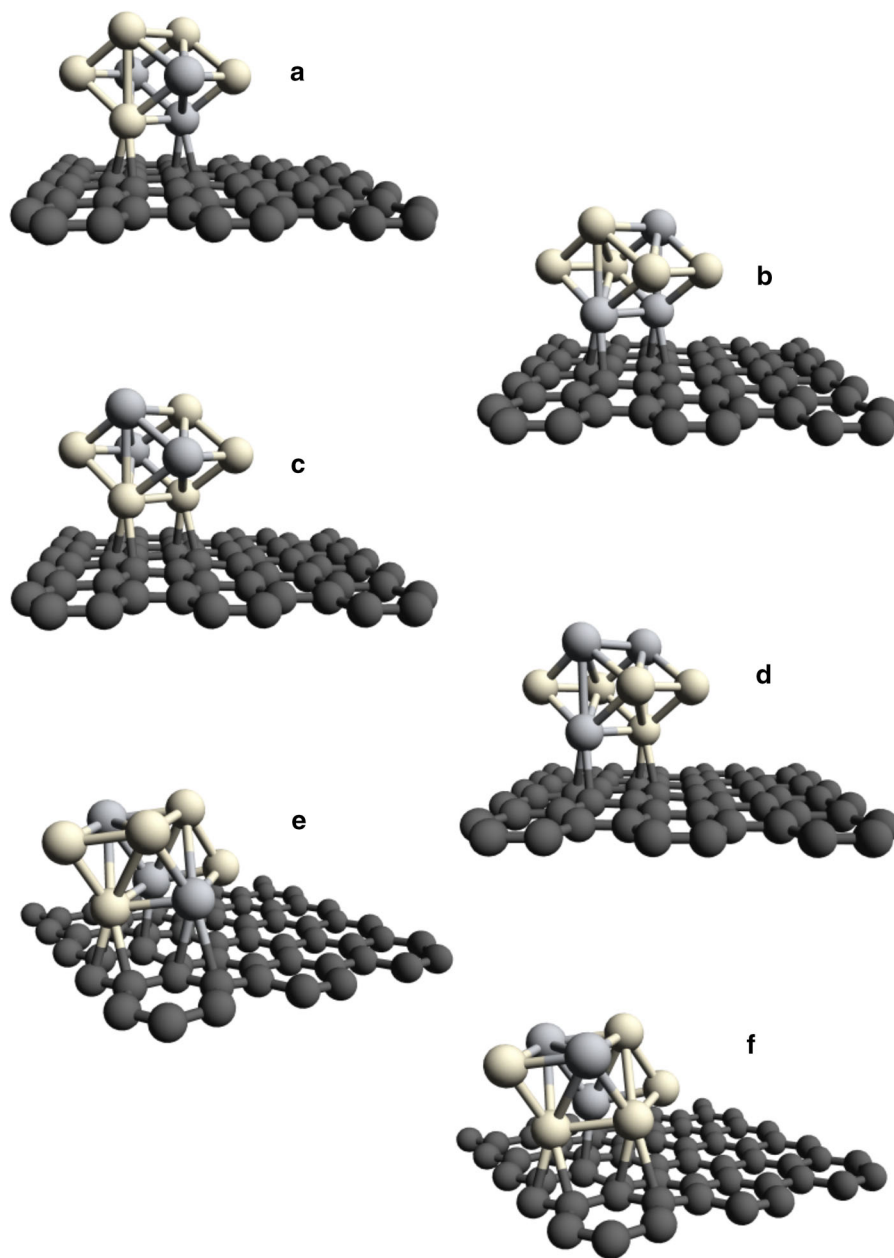
The magnetic moment of  $\text{Mo}_3\text{W}_5$  decreases from 4.00  $\mu_B$ , the value of the free-standing cluster, to values that range from about 1.5 to 3.3  $\mu_B$  when it is supported on the graphene sheet. On the other hand, the magnetic moment on the graphene sheet ranges from about  $-0.03$  to 0.13  $\mu_B$ . It is interesting to note that the total magnetic moment of the system is smaller than the magnetic moment of the free-standing  $\text{Mo}_3\text{W}_5$  cluster indicating that a non-negligible rearrangement takes place in the electronic configuration of the metal cluster after the interaction with the support. The most important electronic configuration rearrangement is observed in conformation (e), although conformations (a) to (d) and (f) to (i) also show an important decrease with respect to the value of 4.00  $\mu_B$  in free-standing  $\text{Mo}_3\text{W}_5$ . Conformations (j) and (k), on the other hand, exhibit the smallest electronic configuration rearrangements according to the magnetic moment value.

Finally, it is observed from Table 1 that all conformations are characterized by a charge transfer from the metal cluster to the graphene sheet that ranges from 0.16 to 0.51  $e^-$ . It is important to note that those conformations with charge transfers above 0.4  $e^-$  involve mainly W atoms binding to the support, conformations (c) and (f) to (i). The exceptions are clearly conformations (j) and (k), which also involve W atoms only but they present the largest number of bonds with the graphene sheet.

### Molecular adsorption of NO on free-standing and on supported $\text{Mo}_3\text{W}_5$

For the sake of simplicity, the molecular adsorption of NO on supported  $\text{Mo}_3\text{W}_5$  is studied considering only the lowest-energy conformation of the  $\text{Mo}_3\text{W}_5$ /graphene system, conformation (a) in Table 1. Despite the fact that some lower-energy conformations of the  $\text{Mo}_3\text{W}_5$ /graphene system could make a non-negligible contribution to the overall picture of the adsorption process, it is expected that the qualitative features will

**Fig. 2** Lower-energy conformations of  $\text{Mo}_3\text{W}_5$  supported on graphene. Only conformations **a–f** are shown. *Black, gray, and white circles* represent C, Mo, and W atoms, respectively

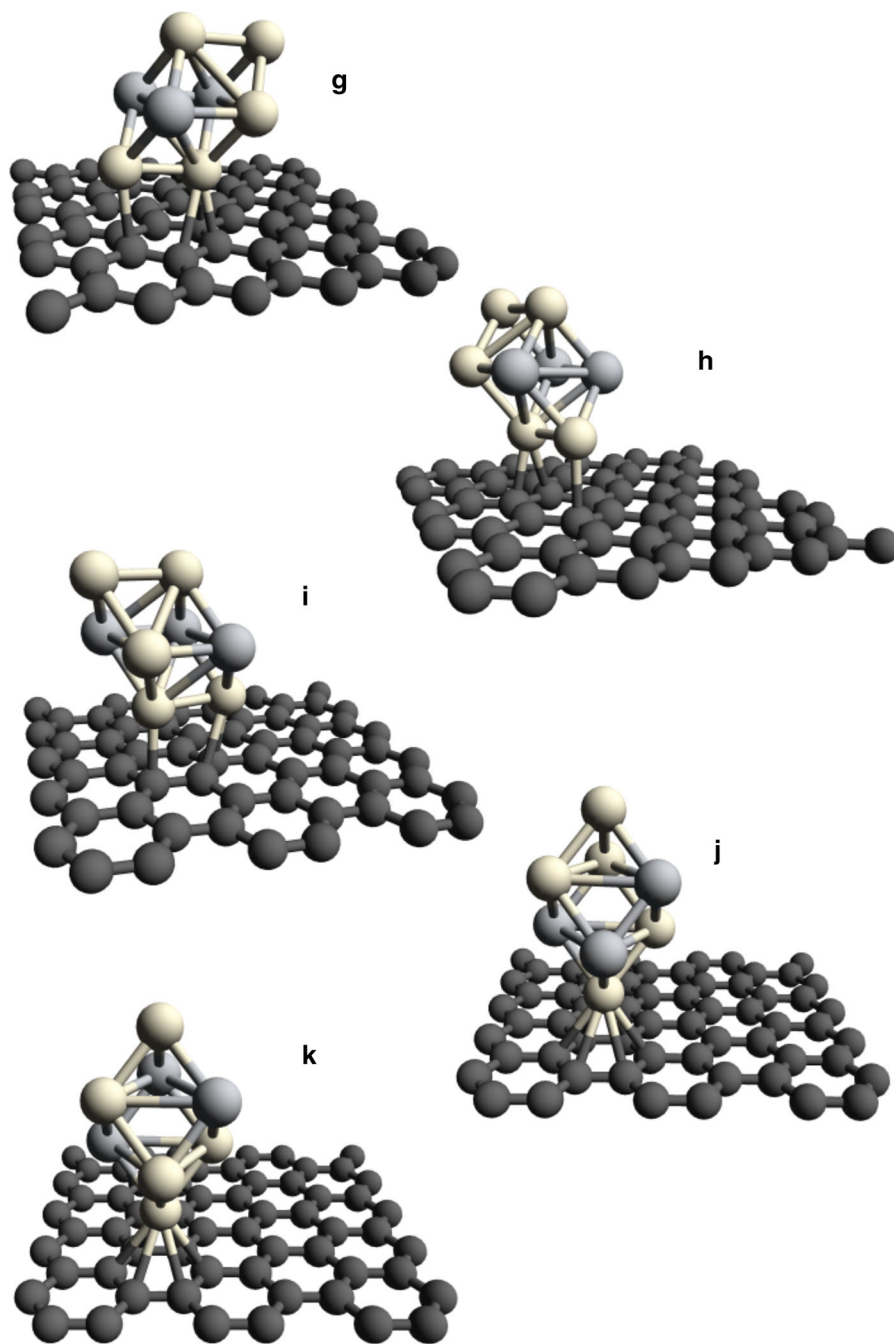


not change appreciably if only the lowest-energy conformation of the whole system is considered.

A large number of adsorption sites both on free-standing and on supported  $\text{Mo}_3\text{W}_5$  were considered. The NO molecule approaches the site both perpendicularly (through the N atom or the O atom) and parallelly (both N and O atoms interact with the site). Only those conformations with the higher adsorption energies are shown and discussed.

The results are shown in Figs. 4 and 5, and are listed in Table 2. Interestingly, the most favored sites for the molecular adsorption of NO on both free and supported  $\text{Mo}_3\text{W}_5$  involve W atoms only. It can also be seen in the figures that the parallel mode in which both the N atom and the O atom bind a W atom is the preferred one, see sites (i-f), (ii-f), (i-s) and (ii-s). Sites (v-f), (vi-f), (viii-f), (v-s), (vi-s), and (viii-s) also exhibit a parallel mode for the interaction of NO with

**Fig. 3** Lower-energy conformations of  $\text{Mo}_3\text{W}_5$  supported on graphene. Only conformations **g–k** are shown. *Black, gray, and white circles* represent C, Mo, and W atoms, respectively



the metal cluster. However, only the N atom binds the W atom as the O-W distance is slightly large to be considered as a bond. Those sites in which the perpendicular mode is observed are characterized by the N atom binding two metal atoms, sites (iii) and (iv), and the O atom binding only one W atom, site (vii).

Adsorption energies, shown in Table 2, are in the range from 2.4 to 4.1 eV when  $\text{Mo}_3\text{W}_5$  is in the gas phase, whereas they are in the range from 2.1 to 4.1 eV when the cluster is supported. Those values indicate a strong interaction between molecular NO and both free-standing and supported  $\text{Mo}_3\text{W}_5$ . Moreover, they seem to suggest that the graphene sheet acting as a

**Table 1** Interaction energy ( $E_{\text{int}}$ , in eV), average interatomic distance in supported  $\text{Mo}_3\text{W}_5$  (M–M, in Å, the total number of bonds in the cluster is shown in parentheses), average interatomic distance in graphene (C–C, in Å), average interatomic distance for the  $\text{Mo}_3\text{W}_5$ /graphene system (M–C, in Å, the total number of bonds formed between  $\text{Mo}_3\text{W}_5$  and graphene is shown in parentheses), magnetic moment of the  $\text{Mo}_3\text{W}_5$ /graphene system ( $\mu$ , in  $\mu_B$ ). Contributions of  $\text{Mo}_3\text{W}_5$

and graphene are given in parentheses), and charge transferred from the bimetallic cluster to the graphene sheet ( $\Delta Q$ , in units of  $e^-$ ) for the different equilibrium geometries found for  $\text{Mo}_3\text{W}_5$  supported on graphene. The equilibrium geometries are labeled according to Figs. 2 and 3. Atomic symbols are used to indicate what atom or atoms interact with graphene, whereas the numbers in parentheses show how many C atoms are involved in the interaction with every metal atom

Conformation	$E_{\text{int}}$	M–M <sup>a</sup>	C–C <sup>b</sup>	M–C	$\mu^c$	$\Delta Q$
(a) MoW (2, 2)	1.499	2.592 (18)	1.455	2.390 (4)	2.470 (2.425, 0.045)	0.335
(b) MoMo (2, 2)	1.467	2.592 (18)	1.454	2.411 (4)	2.227 (2.190, 0.037)	0.156
(c) WW (2, 2)	1.441	2.593 (18)	1.455	2.388 (4)	2.308 (2.273, 0.035)	0.511
(d) MoW (2, 2)	1.417	2.593 (18)	1.454	2.424 (4)	2.913 (2.800, 0.113)	0.304
(e) WMoMo (3, 2, 2)	1.126	2.599 (18)	1.456	2.459 (7)	1.569 (1.491, 0.078)	0.399
(f) WWMo (3, 2, 2)	1.109	2.603 (18)	1.456	2.452 (7)	2.005 (2.034, -0.029)	0.478
(g) WW (1, 3)	1.024	2.596 (18)	1.454	2.503 (4)	2.163 (2.190, -0.027)	0.468
(h) WW (2, 1)	1.005	2.595 (18)	1.454	2.475 (3)	2.680 (2.622, 0.058)	0.438
(i) WW (1, 2)	0.998	2.595 (18)	1.454	2.440 (3)	2.511 (2.494, 0.017)	0.458
(j) W (6)	0.694	2.603 (18)	1.453	2.583 (6)	3.308 (3.221, 0.087)	0.317
(k) W (6)	0.604	2.601 (18)	1.453	2.586 (6)	3.408 (3.282, 0.126)	0.292

<sup>a</sup> The average equilibrium distance in free-standing  $\text{Mo}_3\text{W}_5$  is 2.584 Å, with 18 bonds

<sup>b</sup> The average equilibrium distance in the graphene sheet is 1.445 Å

<sup>c</sup> The magnetic moment of free-standing  $\text{Mo}_3\text{W}_5$  is 4.00  $\mu_B$

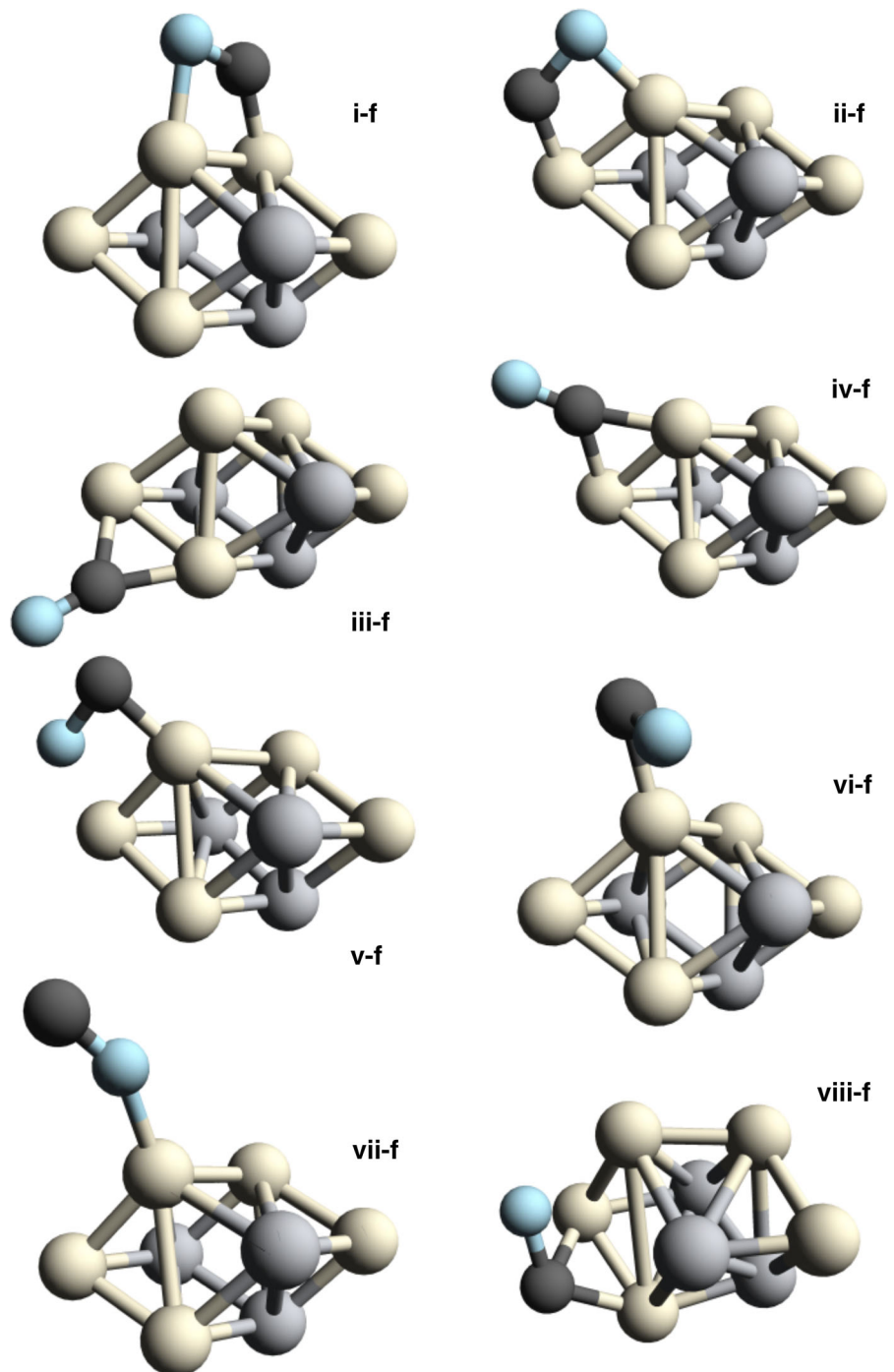
support has little effect on the interaction between NO and  $\text{Mo}_3\text{W}_5$  from an energetic point of view.

The N–O bond distance exhibits an increase larger than 0.3 Å for those sites in which a parallel adsorption mode is observed. The exception is site (vi), for which an increase of only 0.16 Å is found. On the other hand, the N–O bond distance shows an average increase of 0.085 Å when the perpendicular adsorption mode is considered. The average metal-metal distance in both free and supported  $\text{Mo}_3\text{W}_5$  is slightly modified after adsorption. The larger distortions of about 0.024 and 0.023 Å with respect to the free-standing and the supported cluster, respectively, are observed in sites (i-f) and (i-s). In most cases, the  $\text{Mo}_3\text{W}_5$ -graphene average distance shows a decrease of up to 0.03 Å. Only three sites, (i-s), (iii-s), and (vii-s), exhibit a slight increase in the above average distance that reaches the maximum value of 0.11 Å for site (iii-s). The W–N and W–O distances reported in Table 2 are much larger than the calculated equilibrium distances of 1.68 and 1.72 Å for the WN and WO diatomic molecules, respectively.

The magnetic moment of free-standing  $\text{Mo}_3\text{W}_5$  decreases from 4.00  $\mu_B$  to values that range from 0.95

to 3.30  $\mu_B$  when NO is adsorbed. The magnetic moment of NO changes from 1.00  $\mu_B$ , its value when it is isolated in the gas phase, to values that range from -0.13 to 1.71  $\mu_B$  when it is adsorbed on free-standing  $\text{Mo}_3\text{W}_5$ . It is interesting to note that the three sites with the higher adsorption energies, (i-f), (ii-f), and (iii-f), present a magnetic moment of 1.0  $\mu_B$  after NO adsorption. This fact indicates that besides the bond formed between the unpaired electron of NO and one of the four unpaired electrons of  $\text{Mo}_3\text{W}_5$ , the remaining three unpaired electrons of the metal cluster undergo a rearrangement that leads to one unpaired electron only. Is it also possible to think about a two-step process, in which the metal cluster is firstly promoted to a lower-lying excited state with a magnetic moment of 2.00  $\mu_B$  and, secondly, the NO molecule interacts with that excited state by forming a new bond. The resultant magnetic moment of 3.00  $\mu_B$  in sites (iv-f), (vi-f) and (viii-f) indicates that no rearrangement nor promotion take place in those cases and the interaction pattern could be described as the bond formation between the unpaired electron of the NO molecule and one of the four unpaired electrons of  $\text{Mo}_3\text{W}_5$ . Finally, it is worth noting that the resultant

**Fig. 4** Lower-energy conformations of molecular NO adsorbed on free-standing  $\text{Mo}_3\text{W}_5$ . Small black and gray circles represent N and O atoms, respectively. Large gray and white circles represent Mo and W atoms, respectively

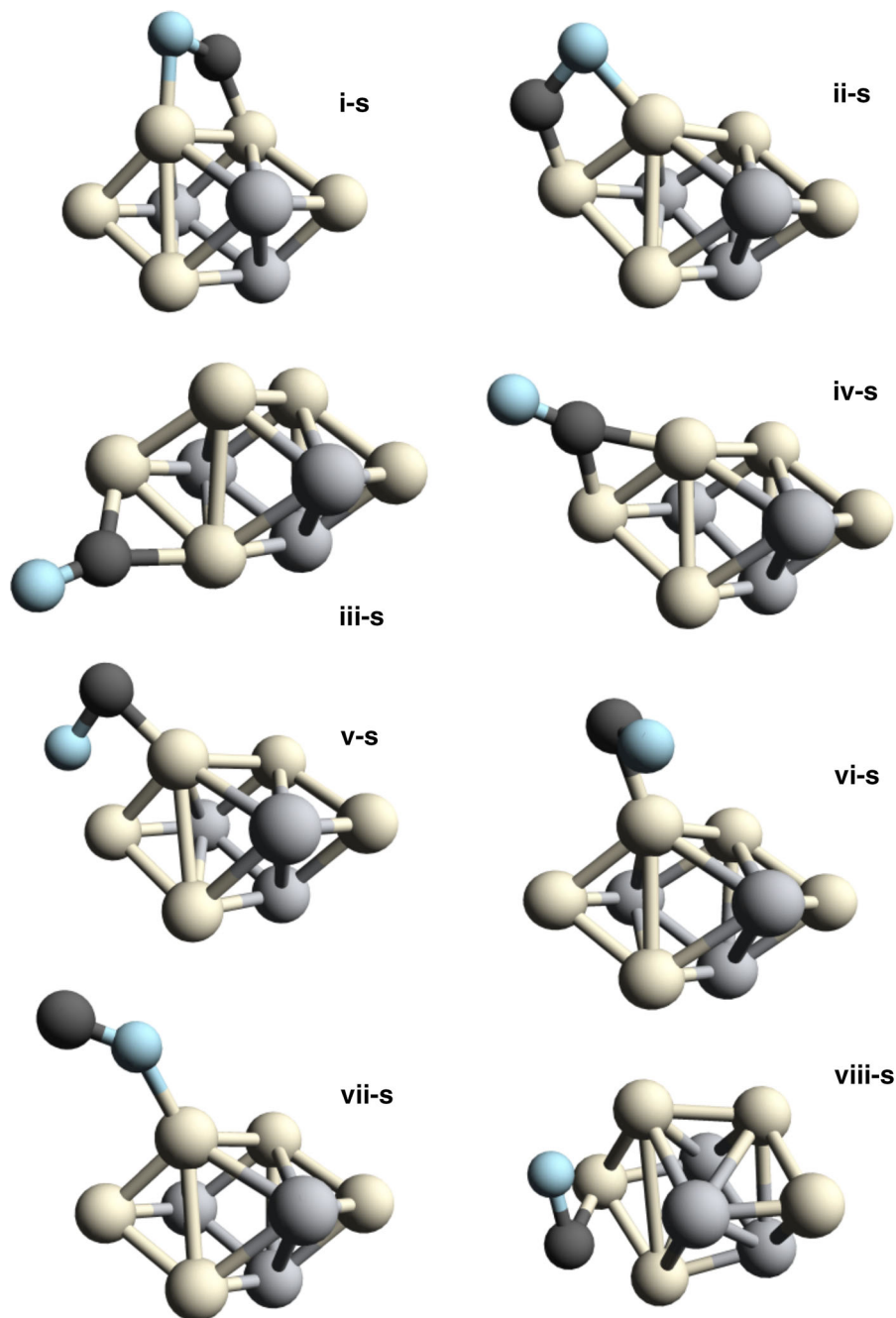


magnetic moment of  $5.00 \mu_B$  in site (vii-f), in which NO adsorbs on-top on a W atom through its O atom, is consistent with the usual description of the NO molecule with the unpaired electron localized on the N atom. Thus, no bonds are formed and the magnetic

moments of NO and  $\text{Mo}_3\text{W}_5$  simply add up to give the resultant value of  $5.00 \mu_B$ . On the other hand, the magnetic moment of the graphene-supported metal cluster diminishes from  $2.425 \mu_B$ , its value in conformation (a), see Table 1, to values that are found



**Fig. 5** Lower-energy conformations of molecular NO adsorbed on graphene-supported  $\text{Mo}_3\text{W}_5$ . *Small black and gray circles represent N and O atoms, respectively. Large gray and white circles represent Mo and W atoms, respectively. Graphene support is not shown*



between 0.00 and  $1.40 \mu_B$  after NO adsorption. The magnetic moment of NO changes from  $1.00 \mu_B$  to values that range from 0.00 to  $1.73 \mu_B$  when it is adsorbed on supported  $\text{Mo}_3\text{W}_5$ . The small magnetic moment induced on the graphene sheet after interaction with  $\text{Mo}_3\text{W}_5$ , see Table 1, undergoes negligible changes after NO adsorption. As expected, the interaction pattern is much more complex when the

graphene sheet participates as support than when the metal cluster is isolated. A simple picture, in which a covalent bond is formed between NO and  $\text{Mo}_3\text{W}_5$  and no electron rearrangements occur, would lead to a resultant magnetic moment of about  $1.4 \mu_B$ . Interestingly, that value is observed in site (iii-s). For the other sites, the resultant magnetic moment is smaller than  $1.4 \mu_B$ , indicating that some non negligible electron

**Table 2** Adsorption energy ( $E_{\text{ads}}$ , in eV), average interatomic distance in both free-standing and supported  $\text{Mo}_3\text{W}_5$  (M–M, in Å), average interatomic distance in the  $\text{Mo}_3\text{W}_5$ /graphene system (M–C, in Å), average interatomic distances for  $\text{Mo}_3\text{W}_5$ -NO (M–N and M–O, in Å), interatomic distance in NO (N–O, in Å), magnetic moments of the  $\text{Mo}_3\text{W}_5$ /graphene +

NO system ( $\mu$ , in  $\mu_{\text{B}}$ ). Contributions of  $\text{Mo}_3\text{W}_5$ , graphene and NO are given in parentheses, and charge transferred from the bimetallic cluster to NO ( $\Delta Q$ , in units of  $e^-$ ) for the different equilibrium geometries found for the adsorption of NO on both free-standing and graphene-supported  $\text{Mo}_3\text{W}_5$ . The equilibrium geometries are labeled according to Figs. 4 and 5

Conformation	$E_{\text{ads}}^{\text{a}}$	M–M <sup>b</sup>	M–C <sup>c</sup>	M–N <sup>d</sup>	M–O <sup>d</sup>	N–O <sup>e</sup>	$\mu^{\text{f}}$	$\Delta Q$
(i-f)	4.136	2.608	–	1.918 (1)	1.998 (1)	1.515	1.003 (1.058, –, –0.055)	0.74
(ii-f)	4.061	2.603	–	1.907 (1)	1.973 (1)	1.543	1.005 (0.958, –, 0.047)	0.72
(iii-f)	3.520	2.596	–	2.038 (2)	–	1.284	1.000 (0.961, –, 0.039)	0.58
(iv-f)	3.470	2.599	–	2.043 (2)	–	1.284	3.000 (2.927, –, 0.073)	0.57
(v-f)	3.378	2.603	–	1.902 (1)	–	1.561	1.000 (1.138, –, –0.138)	0.68
(vi-f)	3.216	2.599	–	2.009 (1)	–	1.386	3.000 (2.238, –, 0.762)	0.51
(vii-f)	2.420	2.588	–	–	1.989 (1)	1.299	5.000 (3.290, –, 1.710)	0.42
(viii-f)	2.370	2.588	–	2.005 (1)	–	1.567	3.000 (3.028, –, –0.028)	0.82
(i-s)	4.095	2.615	2.424	1.945 (1)	2.005 (1)	1.504	0.000 (0.000, 0.000, 0.000)	0.75
(ii-s)	4.091	2.614	2.388	1.915 (1)	1.975 (1)	1.538	0.498 (0.457, –0.007, 0.046)	0.73
(iii-s)	3.131	2.604	2.500	2.034 (2)	–	1.286	1.398 (1.397, –0.014, 0.015)	0.57
(iv-s)	3.476	2.608	2.388	2.040 (2)	–	1.286	1.059 (1.022, 0.011, 0.026)	0.59
(v-s)	3.523	2.614	2.386	1.902 (1)	–	1.553	0.000 (0.000, 0.000, 0.000)	0.98
(vi-s)	3.146	2.588	2.366	2.004 (1)	–	1.372	0.351 (0.311, 0.054, –0.014)	0.47
(vii-s)	2.080	2.603	2.405	–	2.006 (1)	1.310	2.480 (0.782, –0.031, 1.729)	0.43
(viii-s)	2.395	2.592	2.360	1.998 (1)	–	1.567	1.000 (0.957, 0.031, 0.012)	0.82

<sup>a</sup>  $E_{\text{ads}}^{\text{free}}$ , Eq. 2, for the free-standing case and  $E_{\text{ads}}^{\text{supp}}$ , Eq. 3, for the graphene-supported one

<sup>b</sup> The average equilibrium distance in free-standing  $\text{Mo}_3\text{W}_5$  is 2.584 Å, whereas the average distance in supported  $\text{Mo}_3\text{W}_5$  is 2.592 Å, see Table 1

<sup>c</sup> The average equilibrium distance between  $\text{Mo}_3\text{W}_5$  and the graphene sheet is 2.390 Å

<sup>d</sup> The number of M–N and M–O bonds are indicated in parentheses

<sup>e</sup> The equilibrium distance in NO is 1.212 Å

<sup>f</sup> The magnetic moment of free-standing  $\text{Mo}_3\text{W}_5$  and graphene-supported  $\text{Mo}_3\text{W}_5$  in conformation (a) are 4.00 and 2.425  $\mu_{\text{B}}$  (see Table 1), respectively. The magnetic moment of free NO is 1.00  $\mu_{\text{B}}$

rearrangements take place after adsorption. The only exception is site (vii-s), in which NO adsorbs on-top on a W atom through its O atom and the resultant magnetic moment is 2.5  $\mu_{\text{B}}$ . This case is similar to the one found in site (vii-f).

Finally, it is observed from Table 2 that all conformations are characterized by a charge transfer from free-standing and supported  $\text{Mo}_3\text{W}_5$  to the NO molecule that ranges from 0.43 to 0.98  $e^-$ . It is seen that those sites with the larger charge transfers are also the sites in which the activation of the N–O bond is more pronounced. Those sites are characterized by a parallel adsorption of the NO molecule.

## Conclusions

The  $\text{Mo}_3\text{W}_5$  cluster interacts with the graphene sheet preferably through W atoms, which form up to three bonds with the support. Conformations in which one W atom forms up to six bonds with the graphene sheet are much less favored from an energetic point of view. Interaction energies are in the range from 0.6 to 1.5 eV. The amount of charge transferred from the metal cluster to the support ranges from 0.4 to 0.5  $e^-$  for those conformations in which W atoms bind to the graphene sheet. An important decrease in the magnetic moment of the metal cluster with respect to its free-

standing value is observed for those sites in which the bonding pattern to the support is dominated by W atoms. Geometric distortions, both in the metal cluster and in the graphene sheet, are negligible.

The NO molecule adsorbs on sites that involve W atoms only, both for the free-standing and the supported metal cluster. Adsorption energies range from 2 to 4 eV. No appreciable differences are observed in the adsorption pattern when the free-standing and the supported cases are compared. A parallel mode, in which the N and O atoms bind a W atom each is the preferred mode from an energetic point of view. Also, in those cases, the N–O bond becomes more activated. Other sites, in which the N atom binds a W atom, also show an important activation of the N–O bond. However, those sites are much less preferred from an energetic point of view. The change in the magnetic moments indicates that some rearrangement takes place in the electronic configuration of the metal cluster after NO adsorption. Moreover, in most cases, the NO molecule becomes a closed-shell species when it is adsorbed both on free-standing and supported  $\text{Mo}_3\text{W}_5$ , suggesting that its unpaired electron is involved in a bond with the substrate. As expected, an important amount of electronic charge is transferred both from the free-standing and from the supported metal cluster to NO. The amount of charge transferred seems to be closely related to the activation of the N–O bond.

In summary, the  $\text{Mo}_3\text{W}_5$  cluster presents an important catalytic activity to adsorb the NO molecule and for activating the N–O bond, facilitating its later dissociation. Present results indicate that a graphene sheet used as support for the metal cluster has little effect on the catalytic activity. The most important effects of the support could be related to some rearrangements of the electronic configuration in the metal cluster, that are responsible for changes in the magnetic moments after adsorption. However, those rearrangements seem to play a negligible role in the activity of  $\text{Mo}_3\text{W}_5$  to adsorb and activate the NO molecule.

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