Adsorptions of Ni$_8$ Cluster on the Regular and Defect Sites of the MgO(001) Surface

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The adsorption of Ni$_8$ clusters on the anionic (Mg$_{25}$O$_{24}$$^{0/+/2+}$, F$_s$$^{0/+/2+}$) and cationic (Mg$_{24}O_{25}$$^{0/-/2-}$, V$_s$$^{0/-/2-}$) vacancies, as well as on the regular sites (Mg$_{25}$O$_{25}$, Mg^{2+} and NiMg$_{24}$O$_{25}$, Ni^{2+}) of the MgO(001) surface has been investigated at the PW91/DND level of density functional theory. On the basis of the computed adsorption energies, the metal deposition has the decreasing order of Ni$_8$/V$_s$ > Ni$_8$/V$_s$$^-$ > Ni$_8$/V$_s$$^{2-}$ > Ni$_8$/F$_s$$^{2+}$ ≈ Ni$_8$/ Ni^{2+} ≈ Ni$_8$/F$_s$$^+$ ≈ Ni$_8$/Mg^{2+} > Ni$_8$/F$_s$ > Ni$_8$/O^{2-}. Strong electron and charge transfers are found between Ni$_8$ cluster and vacancies or regular sites. The electronic property of the vacancies has been analyzed.

Introduction

The study of metal clusters supported on oxides is of central interest for catalytic applications, such as CO$_2$ reforming of CH$_4$. In catalytic studies, however, relatively large-sized metal particles from 10 to 100 nm are usually deposited by chemical means on inert inorganic substrates.[1] This large size makes the detailed investigations on the chemical and physical properties of the supported catalysts impossible with the available computational capacity. Recently, some excellent theoretical studies on metal adsorptions on oxides have been performed by the study of microclusters or atoms grown on simple crystal models.[1−24]

There is extensive experimental evidence that the seeds of the cluster growth on an oxide surface are the defect sites, in particular the vacancies.[25] Some models have been developed to investigate the adsorption of metal atoms and clusters on regular sites and vacancies of oxide surfaces, such as MgO(001). According to the missing atom or ion, the following nomenclature is used: F$_s$ (missing neutral O), F$_s$$^+$ (missing O$^-$), F$_s$$^{2+}$ (missing O^{2-}), V$_s$ (missing neutral Mg), V$_s$$^-$ (missing Mg$^+$), and V$_s$$^{2-}$ (missing Mg^{2+}).[26] Recently, theoretical studies have been performed on the interaction of Rb, Pd, Ag, Cu, Ni, and Co atoms and/or clusters with these surface sites. Many computational studies focus on the metal adsorption on regular surface sites, and a few aim at the adsorption on the F$_s$ centers.

The computational results[4] indicated that the neutral F$_s$ center of MgO(001) is rather less reactive, as their electronic structure resembles that of the regular surface. The F$_s$$^+$ centers exhibit a relatively large electron affinity (5.4 eV), indicating a propensity for ionization of metal Rb atoms, whereas the electron affinity of the F$_s$$^{2+}$ centers is so high that all metal atoms considered are ionized when interacting with such a site, and this can be ascribed to the positive charge at the local vacancy. Fewer studies focus on the adsorption of the metal atoms and clusters

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on V$_s$ centers of the MgO(001) surface. Furthermore, no general comparison study is found on the adsorption of Ni clusters on all the F$_s$, V$_s$, and regular sites of the MgO surface.

In this work we have carried out density functional calculations of Ni$_8$ cluster adsorption on the anionic (F$_s$, F$_s$$^+$, and F$_s$$^{2+}$; the surface has positive charge), and cationic (V$_s$, V$_s$$^-$, and V$_s$$^{2-}$; the surface has negative charge) vacancies and the regular sites (surface is formally not charged). The structural and energetic properties and electronic distribution are discussed. Our aims are (i) the analysis of the bonding of Ni$_8$ clusters with surface anionic, cationic vacancies, and regular sites and (ii) the geometric and electronic effects of the different sites of the MgO(001) surfaces to the Ni$_8$ clusters.

Methods and Models

All calculations were performed with the program package DMOL^3 in Materials Studio (version 2.2) of Accelrys. We used the double-numeric quality basis set with a set of d-functions (DND) and all electrons for the calculation. The generalized gradient corrected (GGA) functional by Perdew and Wang (PW91)[27] was employed. The Fermi smearing of 0.0002 au (1 au = 27.2116 eV) and the real space cutoff of 5.5 Å were used to improve computational performance. For the numerical integration, we used the FINE quality mesh size, and the tolerances of energy, gradient, and displacement convergence are 2 × 10^{-5} au, 4 × 10^{-3} au/Å, and 5 × 10^{-3} Å, respectively. All calculations were performed in spin polarization. The properties were calculated at the same level of theory.

For preventing the overmuch geometrical changes in the adsorption process, the D_{4d} symmetrical Ni$_8$ cluster was used. This cluster can be considered as a double-layered structure with four Ni atoms in each layer in square form (Figure 1). This is similar to the model by Giordano^3 using C_{4v} Ni$_8$ for adsorption. Although the D_{4d} Ni$_8$ cluster does not correspond to the absolute minima (D_{2d})[28] on the potential energy surface, it simplifies the analysis of results. In contrast to the monolayered model, this double-layered cluster has a reasonable size for a more realistic model and for effective computation. There are two steps for Ni/MgO catalyst (10−100 nm sized) formation; nucleation and growth of Ni on the MgO surface. Although the Ni$_8$ is smaller
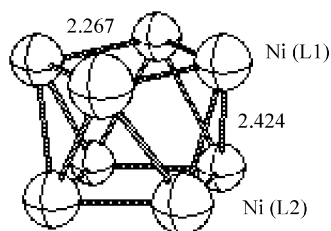
Figure 1. PW91/DND Ni$_8$ clusters (D_{4d}).

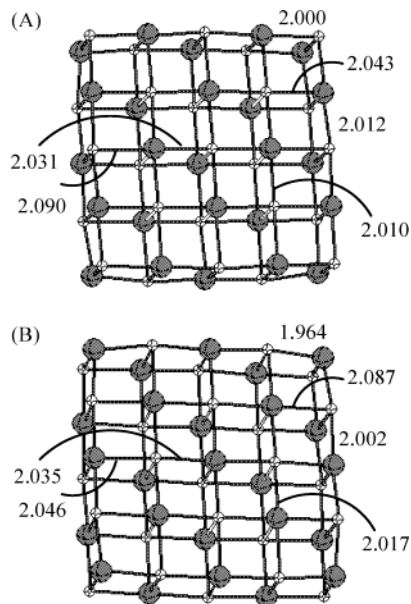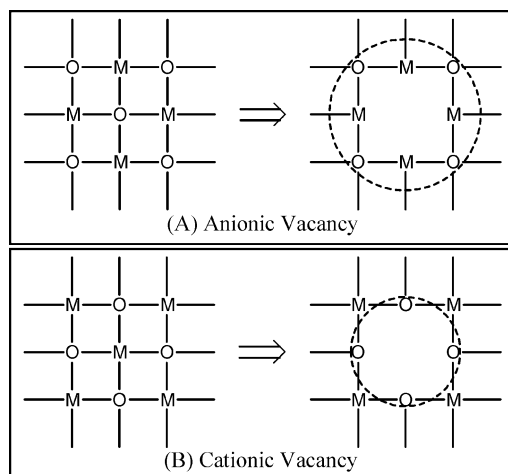**Figure 2.** PW91/DND optimized Mg$_{25}$O$_{25}$ structure (small atom for O and large atom for Mg).

Figure 3. Formation of the vacancies on the MgO(001) surface.

than the real size of catalyst, it can reflect the nucleation step and the subsequent first growth step. This model can provide qualitative insight into the changes of metal surface by MgO(001) surface.

The regular sites of the MgO(001) surface were modeled by a double-layered Mg$_{25}$O$_{25}$ thin film, as shown in Figure 2. Removal of the center O (O$^-$ or O^{2-}) at the front layer of Figure 2A (small atom) results in the anionic vacancy model (F$_s$, F$_s^+$, and F$_s^{2+}$), whereas that of the center Mg (Mg$^+$ or Mg^{2+}) at the front layer of Figure 2B (large atom) leads to the cationic vacancy model (V$_s$, V$_s^-$, and V$_s^{2-}$). This relationship is shown in Figure 3. The Ni$_8$ cluster can be adsorbed at the centers of the regular and vacancy models. For the neutral and anionic

vacancies, the four Ni$_4$ (L2) atoms interact with four oxygen atoms with an oxygen atom at the face center (neutral and anionic vacancy). In this case, the four oxygen atoms, which are connected by Mg atoms, have a separation of roughly doubled Mg−O distance. For the neutral and cationic vacancies, the Ni$_4$ (L2) atoms interact with four oxygen atoms with a magnesium atom at the face center (neutral and cationic vacancies). In this case, the four oxygen atoms have a separation of roughly 1.414 times the Mg−O distance. This indicates that the cationic vacancy should have stronger adsorption interaction than the anionic alternative. The adsorption energy (E_{ads}) is defined as the difference between the adsorbed complex (E_{com}) and the sum of the separated Ni$_8$ cluster (E_{Ni}) and vacancy or regular model (E_{sub}) as substrate, $E_{ads} = E_{com} - (E_{Ni} + E_{sub})$. According to this definition, the more negative the E_{ads}, the stronger the adsorption.
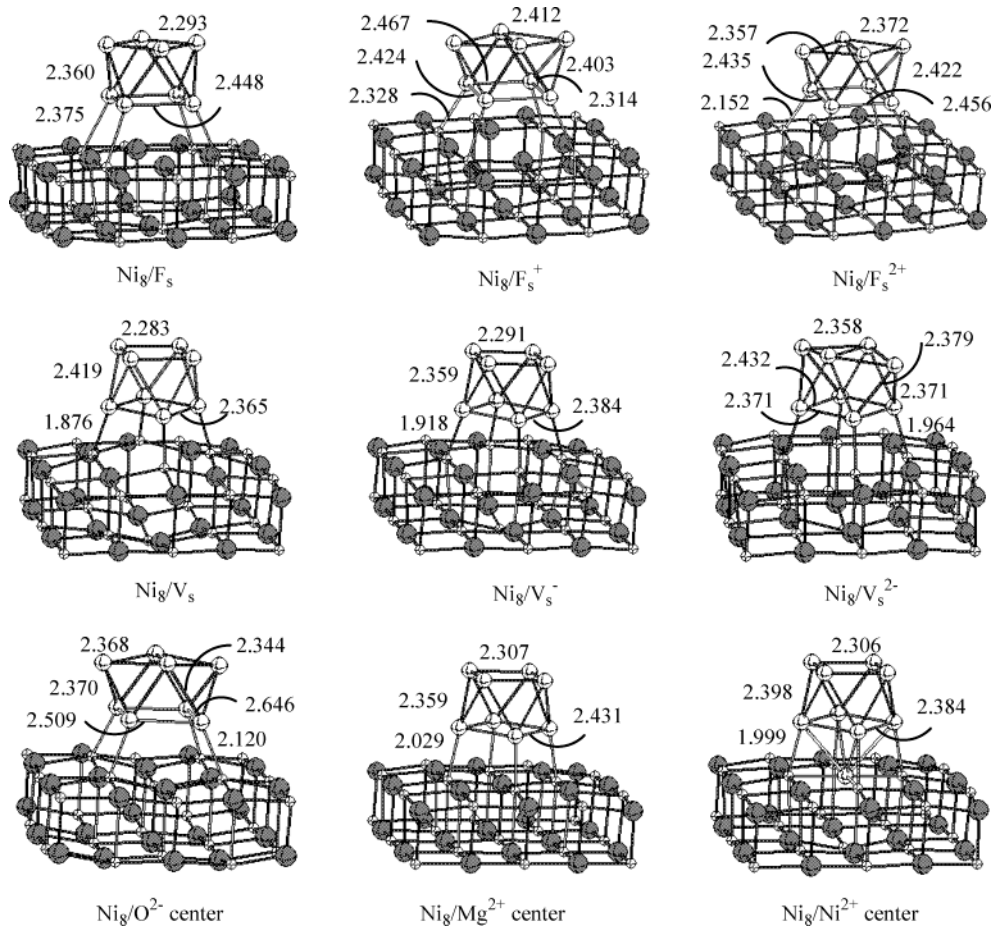
Results and Discussion

(a) Anionic Vacancy Models (Ni$_8$/Mg$_{25}$O$_{24}$, F$_s^{0/+/2+}$). As shown in Figure 1, there are two individual Ni−Ni distances in the D_{4d} symmetrical cluster, 2.267 and 2.424 Å, respectively. In Figure 2, the optimized Mg−O bond lengths (1.964−2.090 Å) of the fully relaxed Mg$_{25}$O$_{25}$ model are close to the experimental bulk-determined value of 2.104 Å;[29] this shows the reasonable quality of the method employed. Figure 4 shows the adsorbed regular and vacancy models. The PW91/DND optimized distances are listed in Table 1. The energetic data of the Ni$_8$ cluster adsorbed on the MgO(001) regular and defect sites are listed in Table 2.

For the adsorption between the Ni$_8$ cluster and the F$_s$ vacancy (Ni$_8$/F$_s$), the Ni−O distance of 2.375 Å is very long, and this is due to the rather large O−O separation, which is nearly the doubled Mg−O distance, as shown in Figure 3 for the anionic vacancy model. This long distance indicates a very weak interaction in Ni$_8$/F$_s$, as also found by other studies.[3,30]

With the increased positive charge at the vacancy, the Ni−O distance decreases in the order Ni$_8$/F$_s$ (2.375 Å) > Ni$_8$/F$_s^+$ (2.328 Å) > Ni$_8$/F$_s^{2+}$ (2.152 Å). This indicates the increased interaction of Ni$_8$ cluster and the anionic vacancy with the increased positive charge at the local vacancies, and this is also supported by the computed adsorption energies in the order Ni$_8$/F$_s$ (−2.49 eV) < Ni$_8$/F$_s^+$ (−3.24 eV) < Ni$_8$/F$_s^{2+}$ (−3.48 eV). This agrees with the findings on reactivity of anionic vacancies.[30] The computed adsorption energies agree with the available theoretical data (Table 2).[3]

(b) Cationic Vacancy Models (Ni$_8$/Mg$_{24}$O$_{25}$, V$_s^{0/-/2-}$). In addition to the anionic vacancy models, we also calculated the adsorption of Ni$_8$ clusters on the cationic vacancies. As given in Table 1, the Ni−O distance increases with the increased negative charge at the vacancy, i.e., 1.876 Å (Ni$_8$/V$_s$), 1.918 Å (Ni$_8$/V$_s^-$), and 1.964 Å (Ni$_8$/V$_s^{2-}$), indicating that the interaction between the Ni$_8$ cluster and the cationic vacancy decreases with the increased negative charge in the sequence Ni$_8$/V$_s$ > Ni$_8$/V$_s^-$ > Ni$_8$/V$_s^{2-}$. This is reflected by the computed adsorption energies in the same order. This behavior is just in contrast to the anionic vacancy model.

Comparing the anionic and cationic vacancies shows that adsorption of Ni$_8$ clusters on the cationic vacancies has a shorter Ni−O bond length and larger adsorption energies than that on the anionic vacancies. This indicates that the Ni$_8$ clusters prefer to adsorb on cationic vacancies. As in Figure 3, the four oxygen atoms surrounding the anionic vacancies have a separation of roughly doubled Mg−O distance, more than 4 Å, which is too large for Ni$_8$ cluster adsorption. Comparatively, the cationic

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2.293
2.360
2.448
2.375
Ni$_8$/F$_s$

2.467
2.424
2.412
2.328
2.403
2.314
Ni$_8$/F$_s^+$

2.357
2.435
2.372
2.152
2.422
2.456
Ni$_8$/F$_s^{2+}$

2.283
2.419
1.876
2.365
Ni$_8$/V$_s$

2.291
2.359
1.918
2.384
Ni$_8$/V$_s^-$

2.358
2.432
2.371
2.379
2.371
1.964
Ni$_8$/V$_s^{2-}$

2.368
2.370
2.509
2.344
2.646
2.120
Ni$_8$/O^{2-} center

2.307
2.359
2.029
2.431
Ni$_8$/Mg^{2+} center

2.306
2.398
1.999
2.384
Ni$_8$/Ni^{2+} center

Figure 4. Structures of Ni$_8$/MgO optimized at PW91/DND (small atom for O and large atom for Mg).

TABLE 1: Calculated Bond Lengths (R, Å) of Ni$_8$ Clusters on Regular and Defect Sites of the MgO (001) Surface

	$R_{(Ni(L1)-Ni(L1))}$	$R_{(Ni(L2)-Ni(L2))}$	$R_{(Ni(L1)-Ni(L2))}$	$R_{(Ni(L2)-O)}$
Ni$_8$ (D_{4d})	2.267	2.267	2.424	
Ni$_8$/F$_s$ (C_{4v})	2.293	2.448	2.360	2.375
Ni$_8$/F$_s^+$ (C_{2v})	2.412	2.424	2.403	2.328
		2.467	2.314	
Ni$_8$/F$_s^{2+}$ (C_{2v})	2.372	2.435	2.422	2.152
		2.456	2.357	
Ni$_8$/V$_s$ (C_{4v})	2.283	2.365	2.419	1.876
Ni$_8$/V$_s^-$ (C_{4v})	2.291	2.384	2.359	1.918
Ni$_8$/V$_s^{2-}$ (C_{2v})	2.358	2.432	2.371	1.964
		2.371	2.379	
Ni$_8$/O^{2-} (C_{2v})	2.368	2.646	2.370	2.120
		2.509	2.344	
Ni$_8$/Mg^{2+} (C_{4v})	2.307	2.431	2.359	2.029
Ni$_8$/Ni^{2+} (C_{4v})	2.306	2.384	2.398	1.999

TABLE 2: Calculated Energetic Parameters of the Ni$_8$ Cluster Adsorbed on the MgO (001) Regular and Defect Sites^a

	E_{com} (au)	E_{sub} (au)	E_{ads} (eV)
Ni$_8$/F$_s$	−18879.13126	−6810.56389	−2.49 (−2.79)^b
Ni$_8$/F$_s^+$	−18879.00650	−6810.41125	−3.24 (−2.86)^b
Ni$_8$/F$_s^{2+}$	−18878.76570	−6810.16187	−3.48
Ni$_8$/V$_s$	−18754.36637	−6685.58848	−8.21
Ni$_8$/V$_s^-$	−18754.42529	−6685.71471	−6.38
Ni$_8$/V$_s^{2-}$	−18754.40871	−6685.73954	−5.26
Ni$_8$/O^{2-}	−18954.51355	−6885.97018	−1.83 (−1.06)^b
Ni$_8$/Mg^{2+}	−18954.56303	−6885.97018	−3.18
Ni$_8$/Ni^{2+}	−20262.97490	−8194.37744	−3.30

^{a} $E(Ni_8) = -12068.47601$ au, $E(Mg_{25}O_{25}) = -6885.97018$ au. ^{b} Taken from ref 3.

vacancies give a relatively small O–O distance, about 2.9 Å, which is close to the Ni–Ni distances 2.267 Å and fit for Ni$_8$ cluster adsorption.

(c) Regular Sites (Ni$_8$/Mg$_{25}$O$_{25}$, Mg^{2+}/O^{2-}) and Ni^{2+} Sites (Ni$_8$/NiMg$_{24}$O$_{25}$). For comparison, we also calculated the interaction between Ni$_8$ and the regular site (Ni$_8$/Mg^{2+} and Ni$_8$/O^{2-}), and the resulting Ni–O distance of Ni$_8$/Mg^{2+}, 2.029 Å, is shorter than those of the Ni$_8$/O^{2-} model, 2.120 Å. This difference is also reflected by the computed adsorption energies of −3.18 vs −1.83 eV, respectively. It indicates that the Ni$_8$ clusters are preferred to adsorb on the regular face focusing on Mg^{2+} rather than on O^{2-} center. This is due to their geometric differences schematically shown in Figure 3.

On the other hand, the Ni–O distance of Ni$_8$/Mg^{2+} is longer than those of the cationic vacancy model, indicating the stronger interaction between Ni$_8$ and the cationic vacancies than between Ni$_8$ and the regular site. This is in line with the computed adsorption energies (Table 2). In contrast, the Ni–O distance of Ni$_8$/Mg^{2+} is shorter than those of the anionic vacancy model, indicating the weaker interaction between Ni$_8$ and the anionic vacancies than between Ni$_8$ and the regular site. However, the computed adsorption energies for Ni$_8$/Mg^{2+} and Ni$_8$/Ni^{2+} are comparable to those of Ni$_8$/F$_s^{+/2+}$ (−3.18/−3.30 vs −3.24/-3.48 eV, respectively).

There are extensive experimental evidences that nucleation occurs preferentially at low coordinated defect sites, rather than on regular terraces of full-coordinated ions.[25] However, our study shows that not all defect sites are preferred to metal nucleation. The cationic vacancies are easier for metal nucleation than regular sites, whereas the anionic vacancies are relatively less reactive. The latter is also comparable to the regular site.

TABLE 3: Mulliken Atomic Charge (δ) of Ni_8 Clusters on the Regular and Defect Sites of MgO(001), the Multiplicity of Spin States

system	δ (Ni_8)	multiplicity	$N_s{}^a$
Ni_8/F_s	−0.472	7	6
$Ni_8/F_s{}^+$	−0.036	8	7
$Ni_8/F_s{}^{2+}$	+0.316	9	8
Ni_8/V_s	+0.520	9	8
$Ni_8/V_s{}^-$	−0.012	8	7
$Ni_8/V_s{}^{2-}$	−0.476	7	6
Ni_8/O^{2-}	−0.214	7	6
Ni_8/Mg^{2+}	−0.252	7	6
Ni_8/Ni^{2+}	+0.036	5	4
Ni_8	0.000	9	8

^{a} Number of unpaired electrons.

As found by Ferrari and Pacchioni, neutral V_s sites are electron deficient, the metal atoms tend to form a dication and to replace the missing Mg^{2+} in the lattice with large gain in the electrostatic energy.[4] On the basis of this finding, we have calculated the modified metal oxide, in which a Ni^{2+} replaces the central Mg^{2+}. As compared to the regular Ni_8/Mg^{2+}, a shorter Ni−O distance is found, but it is longer than those of the cationic vacancies. Therefore, the interaction of Ni_8/Ni^{2+} is in the range of that of the regular Ni_8/Mg^{2+} and the $Ni_8/Mg_{24}O_{25}$, $V_s{}^{-/2-}$. This is clearly indicated by the calculated adsorption energies (Table 2).

Therefore, by the geometrical and energetic analysis, the stability of the adsorption of Ni_8 supported on the different sites of the MgO(001) surface follows the sequence of Ni_8/V_s > $Ni_8/V_s{}^-$ > $Ni_8/V_s{}^{2-}$ > $Ni_8/F_s{}^{2+}$ ≈ Ni_8/Ni^{2+} ≈ $Ni_8/F_s{}^+$ ≈ Ni_8/Mg^{2+} > Ni_8/F_s > Ni_8/O^{2-}. So the metals are inclined to form a nucleus on cationic vacancies first, then they grow on the nucleus rather than form a new one on regular sites and anionic vacancies.

(d) Electron Distribution. The F_s center forms when a neutral oxygen atom is moved from the MgO(001) surface; two valence electrons are located at the vacancy. Similarly, there is one electron in the $F_s{}^+$ vacancy by removing a single negatively charged oxygen species (O^-). Therefore, the F_s and $F_s{}^+$ sites are metallic with electrons in the magnesium hole (electropositive hole) and can be easily oxidized to lose electrons rather than reduced to obtain electrons. This explains the weak interaction in $Ni_8/F_s{}^{0/+}$ reasonably.

On the cationic vacancies with the removal of atomic Mg and a monocationic Mg^+, there are two electrons in the V_s vacancy and one electron in the $V_s{}^-$ vacancy. Because the cationic vacancy is surrounded by electronegative oxygen atoms (electronegative hole), they can be easily reduced to get electrons, which can be obtained from the Ni_8 cluster. This gives a nice explanation on the computed order of adsorption energies: Ni_8/V_s (−8.21 eV) > $Ni_8/V_s{}^-$ (−6.38 eV) > $Ni_8/V_s{}^{2-}$ (−5.26 eV).

In addition to the qualitative analysis, it is also interesting to compare the charge of the Ni_8 cluster as a function of the property of the supports. Table 3 lists the calculated Mulliken atomic charge of the Ni_8 clusters. Due to the metallic character (electropositive hole) of F_s and $F_s{}^+$, the formed surface vacancies will lose electrons to the Ni_8 cluster. Indeed, the Ni_8 cluster has a negative charge (−0.472) in Ni_8/F_s, indicating an electron transfer from support to Ni_8. The same is also found for $Ni_8/F_s{}^+$, in which the Ni_8 is also negatively charged (−0.036). In contrast, the Ni_8 cluster has a positive charge of 0.316 in $Ni_8/F_s{}^{2+}$, indicating an electron transfer from Ni_8 to support. This is due to the large charge effect of the $F_s{}^{2+}$ vacancy, which has a dicationic hole on the surface.

In the cationic vacancy, electron or charge transfer also takes place. For example, due to its electronegative hole in V_s, the Ni_8 cluster has a positive charge of 0.520 in Ni_8/V_s, indicating a strong electron transfer from Ni_8 to V_s, whereas Ni_8 has a negative charge (−0.476) in $Ni_8/V_s{}^{2-}$ due to the negative charge of the $V_s{}^{2-}$ vacancy surface. As an intermediate case, Ni_8 is only slightly negatively charged (−0.012) in $Ni_8/V_s{}^-$.

In addition to the defect surfaces, we have also compared the charges of the regular sites. In both Ni_8/O^{2-} and Ni_8/Mg^{2+}, the Ni_8 cluster has negative charges (−0.214 and −0.252), indicating the base property of the MgO(001) surface. However, the Ni modified surface changes the surface property considerably, and this is indicated by the positive charge of Ni_8 in Ni_8/Ni^{2+}. Therefore, it is possible to change the physical and chemical properties of supports by modifying the surfaces.

It has been found that the deposition of the Ni cluster on the regular and defective MgO surface is generally accompanied by a small magnetic quenching, e.g., the change of the unpaired electrons or the corresponding multiplicity.[3] As given in Table 3, this effect is also found in our calculations. For the anionic vacancies, there are two valance electrons in the F_s vacancy and one in the $F_s{}^+$ vacancy, these electrons can be easily transferred to the Ni_8 cluster, and corresponding multiplicities are reduced, 7 and 8, respectively, compared with the free Ni_8 cluster. Because there are no free valence electrons in $F_s{}^{2+}$, the multiplicity of the adsorbed Ni_8 in $Ni_8/F_s{}^{2+}$ remains unchanged, despite the strong charge transfer. With increased negative charge on the cationic vacancies, the multiplicity changes from 9 to 7. In both anionic and cationic vacancies, the positively charged Ni_8 cluster on the defect surface has a higher multiplicity of 9 ($Ni_8/F_s{}^{2+}$ and Ni_8/V_s), whereas the negatively charged Ni_8 cluster has a lower multiplicity of 7 (Ni_8/F_s and $Ni_8/V_s{}^{2-}$). The multiplicity of the slightly negatively charged vacancies ($Ni_8/F_s{}^+$ and $Ni_8/V_s{}^-$) has an intermediate value of 8. However, no such direct relationship can be found for the deposition on the regular surfaces. For example, both Ni_8 clusters on the regular surfaces (Ni_8/Mg^{2+} and Ni_8/O^{2-}) are negatively charged, but their multiplicities (7) are higher than that (5) of the Ni doped surface (Ni_8/Ni^{2+}), although the Ni_8 in the former are negatively charged, but slightly positively charged in the latter. Therefore, not only electron transfer but also polarization in the interface can change the multiplicity. There are correlations between the distance in the interface and the multiplicity.

Conclusions

The adsorption of the Ni_8 cluster on the regular and defect sites of the MgO(001) surface of a double-layered $Mg_{25}O_{25}$ thin film has been investigated using the PW91 density functional method. Removal of surface O, O^-, and O^{2-} results in anionic vacancies ($F_s{}^{0/+/2+}$), whereas removal of surface Mg, Mg^+, and Mg^{2+} forms cationic vacancies ($V_s{}^{0/-/2-}$).

Due to its metallic character, the F_s vacancy with two valence electrons ($Mg_{25}O_{24}$, F_s) forms an electropositive hole and can be easily oxidized by losing electrons. This is indicated by the highly negative charges of the Ni_8 cluster, and the computed adsorption energy is exothermic. With increased positive charge at the vacancy, however, $F_s{}^+$ ($Mg_{25}O_{24}{}^+$, $F_s{}^+$) and $F_s{}^{2+}$ ($Mg_{25}O_{24}{}^{2+}$, $F_s{}^{2+}$) have increased exothermic adsorption energies, and this can be ascribed to the decreased electron transfer from support to Ni_8 in $Ni_8/F_s{}^+$, but increased charge transfer from support to Ni_8 or transfer from Ni_8 to support in $Ni_8/F_s{}^{2+}$. As a result, Ni_8 has negative charge in Ni_8/F_s (reduced Ni_8), but positive charge in $Ni_8/F_s{}^{2+}$ (oxidized Ni_8).

In contrast to the anionic vacancies, a much stronger interaction between the cationic vacancies and Ni_8 is found. Due

to its electronegative property, the V$_s$ vacancy (Mg$_{24}$O$_{25}$), which forms an electronegative hole and can be easily reduced by getting electrons, has the largest adsorption energy (Ni$_8$/V$_s$) with the strongest electron transfer from Ni$_8$ to the support. With increased negative charge at the vacancy, however, V$_s^-$ (Mg$_{24}$O$_{25}^-$) and V$_s^{2-}$ (Mg$_{24}$O$_{25}^{2-}$) have decreased, but exothermic adsorption energies. It is interesting to note that Ni$_8$ has a positive charge in Ni$_8$/V$_s$ (oxidized Ni$_8$), but a negative charge in Ni$_8$/V$_s^{2-}$ (reduced Ni$_8$).

On the basis of the computed adsorption energies, the Ni$_8$ cluster prefers to deposit on cationic rather than anionic vacancy. On the regular site, the Ni$_8$ cluster is preferred to deposit over Mg^{2+} rather than over the O^{2-} center. The Ni^{2+} modified surface has an even larger adsorption energy, respectively.

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