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Article

Influence of nickel(II) oxide surface magnetism on molecule adsorption: A first-principles study

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ABSTRACT

The influence of the magnetism of transition metal oxide, nickel(II) oxide (NiO), on its surface reactivity and the dependence of surface reactivity on surface orientation and reactant magnetism were studied by density functional theory plus U calculations. We considered five different antiferromagnetically ordered structures and one ferromagnetically ordered structure, NiO(001) and Ni(011) surfaces, paramagnetic molecule NO, and nonparamagnetic molecule CO. The calculations showed that the dependence of surface energies on magnetism was modest, ranging from 49 to 54 meV/Å² for NiO(001) and from 162 to 172 meV/Å² for NiO(011). On NiO(001), both molecules preferred the top site of the Ni cation exclusively for all NiO magnetic structures considered, and calculated adsorption energies ranged from −0.33 to −0.37 eV for CO and from −0.42 to −0.46 eV for NO. On NiO(011), both molecules preferred the bridge site of two Ni cations irrespective of the NiO magnetism. It was found that rather than the long-range magnetism of bulk NiO, the local magnetic order of two coordinated Ni cations binding to the adsorbed molecule had a pronounced influence on adsorption. The calculated NO adsorption energy at the (↑↑) bridge sites ranged from −0.99 to −1.05 eV, and become stronger at the (↑↑) bridge sites with values of −1.21 to −1.30 eV. For CO, although the calculated adsorption energies at the (↑↓) bridge sites (−0.73 to −0.75 eV) were very close to those at the (↑↑) bridge sites (−0.71 to −0.72 eV), their electron hybridizations were very different. The present work highlights the importance of the local magnetic order of transition metal oxides on molecular adsorption at multi-fold sites.

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1. Introduction

Transition metal oxide (TMO) surfaces currently have a wide range of applications in energy and environmental science, such as catalysts for clean energy conversion, cleanup of air pollutants, and sensors for chemical and biomedical devices [1,2]. Understanding the surface chemistry and struc-

ture–activity relationship of TMOs is therefore important for the further development of these applications [3]. In particular, 3d TMOs are notable because of their involved spin states and magnetism, which is sensitive to surface orientation and particle size [4–7]. For instance, the spin states of Co ions (rather than number of 3d electrons) in perovskite oxides play a critical role in their oxygen evolution activity [8]. In addition to

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oxides, the spin states of molecules such as O₂ influence their corresponding dissociation activity on oxides [9] and even simple metal surfaces [10]. Magnetism can be induced in metal oxides that are paramagnetic in bulk by surface adsorption and reaction [11,12]. It is therefore interesting to study the influence of the spin states and magnetism of oxides on their surface chemistry.

Late 3d transition metal monoxides (MnO, FeO, CoO, and NiO) with cubic rock salt structure (Fm $\bar{3}$ m) [13,14] are of particular importance in the study of antiferromagnetic (AFM) TMOs, and are often considered as model AFM systems. Besides their relatively high Neel temperature (T_N) and chemical stability, their large band gap (E_G) and insulating electronic structure allow their magnetic properties to be accurately described in terms of magnetic moments localized on transition metal cations [15,16]. The anisotropic interaction between neighboring magnetic moments leads to long-range magnetic ordering, known as type-2 antiferromagnetism (AFM2), below T_N [17–20] and stacking of ferromagnetic (FM) (111) planes with opposite spin directions in adjacent layers, as identified by neutron diffraction [21]. Using magnetic exchange force microscopy, the magnetic order of surface nickel ions on the NiO(001) surface has been measured directly in real space [22–26]. Despite the definite AFM order of magnetic ions in the perfect bulk crystal below T_N , the ordering of magnetic ions on the surface can be changed under different conditions. For example, by engineering defects in the lattice of AFM NiO, a FM ordering dislocation can be introduced [27]. When the size of AFM NiO decreases to the nanoscale, the resulting decrease of coordination and lattice distortion can drive the phase transition to a FM-like phase [27,28].

The magnetism of metal ions in late 3d TMOs originates from their partially filled 3d states, which are famous for their highly correlated nature [29]. It remains challenging to accurately describe strongly localized and correlated *d* electrons using standard density functional theory (DFT) approaches such as the local density approximation (LDA) or generalized gradient approximation (GGA) [30,31]. Both the LDA and GGA often fail to predict E_G of these TMOs [32]. For instance, both CoO and FeO were predicted to be metallic. Although NiO and MnO were predicted to have E_G , the calculated values were severely underestimated [33]. Nevertheless, E_G of these materials can be opened in calculations by adding a Hubbard *U* term describing the strong on-site Coulomb repulsion to the LDA or GGA (DFT+*U*) [34,35]. Compared to higher-level theories such as the hybrid functional or many-body perturbation [31,36], DFT+*U* can substantially improve the calculation accuracy without increasing the computational cost, as demonstrated for the adsorption of CO and NO on NiO(001) [37,38]. Simulation of water dissociative adsorption on NiO(111) was reported recently, and the calculation was found to be fairly insensitive to the choice of the DFT+*U* functional [39].

Chemically equivalent oxide surfaces may become inequivalent when considering the different symmetry of various long-range magnetisms. Because surface chemistry is largely decided by local environment (geometry and composition), it is currently unclear how the different magnetisms affect surface

chemistry. Furthermore, the influence of different surfaces on magnetisms is still unknown. This influence may be mediated by reactants with different spin and/or magnetic moments. To clarify these issues, here NiO as a model system is studied by the GGA +*U* method. A number of magnetic phases, including AFM1, AFM2, AFM3, AFM4, AFM5, and FM, are considered. NiO(001) and NiO(110) surfaces are used to study the sensitivity of these magnetic phases to structure. While CO and NO adsorbed on NiO(001) of AFM2 has been studied to verify the DFT+*U* scheme treatment for strongly correlated systems [37,38], here we use the adsorption of paramagnetic molecule NO and nonparamagnetic molecule CO to probe the influence of magnetism on molecule adsorption by NiO surfaces.

2. Computational details

DFT calculations were performed with the Vienna ab initio simulation package (VASP) [40] based on the projected augmented wave (PAW) method [41,42]. The spin-polarized Perdew Burke Ernzerhof (PBE) [43] exchange-correlation functional and on-site Coulomb repulsion *U* term for *d* electrons in the spirit of Hubbard according to Dudarev's approach [35] were used to describe electron exchange and correlation. An effective *U* of 5.3 eV for Ni was used throughout the present work, because it could reproduce well bulk properties and CO/NO adsorption on NiO(001) surfaces [37].

Because partially occupied *d* orbitals are strongly localized at Ni²⁺, a net spin magnetic moment was assigned to each Ni²⁺. For the cubic sublattice of magnetic ions, all magnetic ions having parallel spin means there is FM order (Figure 1(a)). In

Fig. 1. Schematic illustration of NiO ferromagnetism FM (a), antiferromagnetism AFM1 (b), AFM2 (c), AFM3 (d), AFM4 (e) and AFM5 (f). Line cross points represent O, blue balls represent Ni spin up, and white balls represent Ni spin down.

contrast, the series of common AFM configurations of Ni^{2+} AFM1–AFM5 (as shown in Figure 1(b–f)) can be described as oppositely stacked FM layers in direction G with super lattice periodicity p in which Ni^{2+} maintain parallel spin within p layers [44]. Below $T_N = 523$ K, the ground-state magnetic configuration of NiO is AFM2 [21]. We considered AFM1–AFM5 and FM magnetic order as a starting point to construct surfaces with different surface magnetic order by truncation of bulk NiO.

Four layers of an NiO(001) slab ($2\sqrt{2} \times 2\sqrt{2}$) surface supercell and five layers of an NiO(011) slab (4×4) surface supercell were used to model the adsorption of molecules on NiO(001) and NiO(011) surfaces, respectively. Slabs were separated by 12 Å of vacuum with the bottom two layers fixed at the bulk truncated structure, and dipole correction perpendicular to each slab was imposed. The layer thickness and vacuum size were found to converge for adsorption of CO/NO on AFM2. Surface energy was evaluated with symmetric slabs of the minimum surface cell for each surface until they converged to less than 1 meV/Å² with respect to slab thickness. A plane wave cutoff of 400 eV and k-point grids of ($4 \times 4 \times 1$) for NiO(001)-($2\sqrt{2} \times 2\sqrt{2}$) and ($3 \times 2 \times 1$) for NiO(011)-(2×4) were used. Geometrical optimization was performed until the force on relaxed atoms was less than 0.02 eV/Å.

3. Results and discussion

3.1. NiO bulk

Table 1 lists the optimized equilibrium lattice constant, energy difference per NiO formula with respect to the lowest energy state (AFM2), localized magnetic moment on Ni, and band gap for the various magnetic phases considered. The energetically most favorable long-range magnetic phase is AFM2, which is consistent with the structure of NiO below T_N determined by neutron diffraction. The energy difference between different magnetic phases can be as large as 102 meV/NiO. AFM2 has the smallest lattice constant ($a = 4.19$ Å) and magnetic moment of Ni ($m = 1.71 \mu_B$), but the largest E_G of 3.25 eV for the magnetic phases. The present work agrees well with the results of a previous SGGA+U calculation ($a = 4.20$ Å, $m = 1.72 \mu_B$, $E_G = 3.2$ eV) [37]. For the other AFM phases, the lattice constant and magnetic moment increase by 0.02 Å and 0.10 μ_B at most, respectively, but E_G decreases by 1.16 eV. It is clear that the lower the energy of the magnetic phase, the smaller the lattice constant

and magnetic moment and the larger the E_G . These trends originate from the superexchange interaction of the second nearest neighbor (NN) Ni^{2+} , as rationalized in an earlier theory for rock salt transition metal monoxides [33,45].

To understand the origin of the AFM behavior of NiO, we fitted the calculated energy in Table 1 to the Ising model of magnetic moment interaction [19]. The fitting result gives i -th NN magnetic moment exchange pair interactions J_i ($i = 1, 2, 3$, and 4) of 0.71, −15.58, −0.24, and 0.07 meV, respectively. This means that the second NN interaction (J_2) is the dominant interaction and the negative value indicates the preference for AFM order, similar to the behavior of CoO and MnO [18,19]. Because J_1 , J_3 , and J_4 are much smaller than J_2 , the number of second NN pairs determines the relative stability of the various AFM phases. For AFM2, all the second NN pairs are antiparallel, so it is energetically the most favorable state of NiO.

In this work, a Ni atom with an upward (or positive) magnetic moment ($\uparrow$) means that the electron population of the spin-up component is larger than that of the spin-down, whereas a Ni atom with a downward (or negative) magnetic moment ($\downarrow$) means that the electron population of the spin-down component is larger than that of the spin-up. The spin-resolved density of states (SDOS) of Ni ($\uparrow$) in bulk NiO-AFM2 is illustrated in Figure 2. For the $3d_{xy,yz,xz}$ (t_{2g}) band, both the spin-up and spin-down components are distributed in the valence band. Compared with the spin-up component, the electrons in the spin-down component mainly populate the upper/top part of the valence band. For the $3d_{x^2-y^2,z^2}$ (e_g) band, the marked exchange splitting causes the e_g states to be well separated (by ~ 9.69 eV). In particular, the spin-down components are distributed in the conduction band. Most of the spin-up components are distributed in the lower part of the valence band, and a small amount are distributed close to the top of the valence band. The gap between the valence band maximum (VBM) and conduction band minimum (CBM) of the Ni 3d band is 3.23 eV, which is nearly same with as the E_G of bulk NiO (3.25 eV). For Ni($\downarrow$), the corresponding components are simply reversed. As shown below, these features are essential for the hybridization between Ni and CO/NO molecules.

3.2. NiO(001)

3.2.1. Surface properties

For rock salt crystals, the (001) plane is chemically equivalent with (010), (100), (00 $\bar{1}$), (0 $\bar{1}$ 0), and ($\bar{1}$ 00): all belong to the {001} plane family, and the corresponding primitive cell is (1×1). A long-range magnetic phase lowers the corresponding symmetry and decreases the degeneracy of the {001} plane family. The nonequivalent planes depended on the long-range magnetic phase (AFM1–AFM5), as classified in Table 2 and plotted in Figure 3. Each of AFM1, AFM3, AFM4, and AFM5 had two nonequivalent planes, whereas AFM2 had only one nonequivalent plane. This led to nine nonequivalent surfaces with different primitive cells, although they are all chemically equivalent.

Taking AFM1-(100) (Figure 3(b)) as an example, the magnetic moments of the first NN Ni pair are exclusively antiparal-

Table 1

Energy difference per NiO formula with respect to the lowest state (AFM2) (ΔE), equilibrium lattice constant (a), localized magnetic moment on Ni (M), and energy band gap (E_G) of various magnetism phases.

	$\Delta E/\text{meV}$	$a/\text{\AA}$	M/μ_B	E_G/eV
AFM1	101	4.21	1.81	2.20
AFM2	0	4.19	1.71	3.25
AFM3	65	4.20	1.77	2.51
AFM4	61	4.20	1.77	2.26
AFM5	30	4.19	1.74	2.88
FM	91	4.21	1.80	2.09

Fig. 2. Spin-resolved projected density of states (SDOS) for Ni in bulk AFM2 NiO. (a) SDOS projected onto Ni $3d_{xz}$, $3d_{x^2-y^2}$; (b) SDOS projected onto Ni $3d_{xy}$, $3d_{yz}$, $3d_{xz}$; (c) Total SDOS of Ni $3d$. The reference coordinates for DOS projection is shown in inset of (a), where x-axis represents for $[100]$ direction and y-axis for $[010]$ direction.

lel ($\uparrow\downarrow$). Similar behavior was found for AFM3-(001) (Figure 3(d)). In contrast, for AFM1-(001) (Figure 3(a)) and AFM4-(001) (Figure 3(f)), the magnetic moments of the first NN Ni pair are exclusively parallel ($\uparrow\uparrow$). For the remaining five surfaces shown in Figure 3, both the ($\uparrow\downarrow$) and ($\uparrow\uparrow$) configurations coexist in the first NN Ni pairs, forming different surface magnetism patterns. The different local magnetic pairs along with their long-range magnetic phases provide a good playground to investigate the influence of magnetism on surface properties. Figure 4 plots the SDOS of a surface Ni atom ($\uparrow$) from AFM2-(001). The overall features remain the same as that of AFM2 bulk (Figure 2). The main difference is the gap between the VBM and CBM of the Ni $3d$ band, which decreases from the bulk value of 3.23 to 2.81 eV.

The calculated surface energies are presented in Table 2.

Table 2

Nonequivalent surfaces of rock salt NiO{001} family taking into account of magnetism, though in each column the surfaces remain equivalent. Corresponding surface energy γ (meV/Å²) is given, and as reference for FM(001), $\gamma = 50$ meV/Å².

	AFM1		AFM2		AFM3		AFM4		AFM5	
γ	49	50	54	54	51	54	52	52	54	
(001)	(100)	(001)	(001)	(010)	(001)	(010)	(001)	(010)	(001)	(010)
(00 $\bar{1}$)	($\bar{1}00$)	(00 $\bar{1}$)	(00 $\bar{1}$)	(0 $\bar{1}0$)	(00 $\bar{1}$)	(0 $\bar{1}0$)	(00 $\bar{1}$)	(0 $\bar{1}0$)	(00 $\bar{1}$)	(0 $\bar{1}0$)
	(010)	(010)	(010)	(100)		(100)		(100)		(100)
	(0 $\bar{1}0$)	(0 $\bar{1}0$)		($\bar{1}00$)		($\bar{1}00$)		($\bar{1}00$)		($\bar{1}00$)
		(100)	(100)							
		($\bar{1}00$)	($\bar{1}00$)							

The surface energies range from 49 to 54 meV/Å², and the difference between different magnetic phases is less than 5 meV/Å². To rationalize this small variation, we note that the surface energy increases mainly from the cost of Ni–O bond cleavage when creating a new surface. Considering the exchange coupling between magnetic cations, cleavage of the Ni–O bond might introduce an additional cost originating from the loss of the corresponding exchange interaction. Because the exchange interaction between Ni²⁺ is largely determined by J_2 , the estimated cost of breaking the J_2 interaction when creating a new surface is ~ 1.7 meV/Å². Namely, the contribution from the long-range AFM phases to the surface energy is indeed small. Compared to the calculated overall surface energy, the contribution from magnetism ($\sim 3\%$) is negligible.

3.2.2. Adsorption of CO and NO molecules

CO and NO adsorption on these nonequivalent surfaces at a coverage of 0.25 monolayer with respect to surface Ni was

Fig. 3. Top view configuration of various nonequivalent NiO(001) surfaces taking into account of magnetism. Surface primitive cells are marked by frame of red dash line.

Fig. 4. Spin-resolved projected density of states (SDOS) for upward magnetic moment Ni(↑) of clean NiO AFM2(001). (a) SDOS projected onto Ni $3d_{xz}$, $3d_{x^2-y^2}$; (b) SDOS projected onto Ni $3d_{xy}$, $3d_{yz}$, $3d_{xz}$; (c) Total SDOS of Ni $3d$. The reference coordinates for DOS projection is shown in inset of (a), where x -axis represents for $[100]$ direction and y -axis for $[010]$ direction.

studied. Various adsorption sites were considered, and the results for adsorption at the energetically most favorable sites are given in Table 3. For the nonequivalent surfaces considered, calculated CO adsorption energies varied from -0.33 to -0.37 eV, while NO adsorption energies were more exothermic and ranged from -0.42 to -0.46 eV. The small change of adsorption energies (0.04 eV; less than 10%) reveals the weak influence of the long-range magnetic phases on both CO and NO adsorption. The calculated adsorption energies are in good agreement with those obtained from a previous GGA+U calculation on a (001) surface of NiO with AFM2 magnetic order and thermodesorption and infrared experiments (-0.30 to -0.45 eV for CO and -0.52 to -0.57 eV for NO) [37,38,46–48].

Table 3

Magnetism and structure information of CO adsorption on NiO {001}. Magnetic moment (M_{Ni} , M_{CO}) is given in unit of μ_B . Adsorption energy of CO E_{ads} is given in eV. Bond length ($d_{\text{Ni-C}}$) is given in Å.

	$M_{\text{Ni(clean)}}(\uparrow)/\mu_B$	$M_{\text{Ni}}(\uparrow)/\mu_B$	M_{CO}/μ_B	$d_{\text{Ni-C}}/\text{Å}$	E_{ads}/eV
AFM1(001)	1.80	1.78	0.01	2.04	−0.34
AFM1(100)	1.81	1.78	0.02	2.05	−0.34
AFM2(001)	1.72	1.69	0.01	2.07	−0.36
AFM3(001)	1.78	1.76	0.02	2.05	−0.33
AFM3(100)	1.77	1.74	0.01	2.04	−0.34
AFM4(001)	1.78	1.76	0.01	2.05	−0.34
AFM4(100)	1.77	1.74	0.02	2.04	−0.35
AFM5(001)	1.74	1.70	0.01	2.02	−0.37
AFM5(100)	1.75	1.72	0.02	2.04	−0.34
FM(001)	1.80	1.77	0.02	2.05	−0.35

In line with its weak binding strength, CO adsorption induces little change of the magnetism (less than $0.02 \mu_B$) of CO and coordinated Ni atom. As shown in Figure 5(a), CO adsorbed nearly perpendicularly at the top of a Ni atom. The optimized Ni–C bond length varied from 2.02 to 2.07 Å, where a shorter bond length indicates stronger binding. Meanwhile, the C–O bond length of 1.14 Å was the same as that of gas-phase CO. Small tilting of the angle between the Ni–C and C–O bonds could be energetically favorable; however, the variation of the corresponding potential energy surface was less than 10 meV for tilt angles up to 30° [37].

The bonding mechanism between CO and a coordinated Ni atom can be inferred from the corresponding SDOS plotted in Figure 5(b). The hybridization is mainly between the CO 5σ orbital and Ni $3d_{z^2}$ band in the bottom of the valence band (donation). In addition, there is weak hybridization between CO $2\pi^*$ and Ni $3d_{x^2-y^2}$ in the conduction band (back donation). The fact that both hybridizations appear far from the Fermi level rationalizes well the weak binding strength of adsorbed CO.

Fig. 5. CO adsorption on NiO AFM2(001). (a) Adsorption configuration; (b) SDOS of Ni $3d$ and CO $2p$ orbitals; (c) Isosurface view; (d) Section contour view of difference of electron density for CO adsorption. For isosurface view, yellow/green color means electron accumulation/depletion respectively.

Direct visualization of the bonding between CO and Ni can be better seen from the difference of electron density (Figure 5(c) and (d)). Pronounced charge accumulation between CO and coordinated Ni is observed, which indicates the dominating role of the donation interaction in CO adsorption on a NiO(001) surface.

Compared with the case for CO adsorption, NO binds more strongly to Ni with a tilted configuration (Figure 6(a)), in agreement with previous studies of NO adsorption on NiO(100) [38] and transition metal surfaces [49,50]. For instance, on AFM2-(001), the tilt angle is 10.7° for the Ni–N bond and 49.5° for the N–O bond. Depending on the magnetic phase (Table 4), the optimized Ni–N bond length varies in the range of 1.98–2.05 Å, and the configuration with a shorter Ni–N bond length is consistent with stronger binding. The N–O bond length (1.17–1.18 Å) is nearly the same as that of the gas phase (1.17 Å). After NO adsorption, the magnetic moments of NO and coordinated Ni decrease by about 0.10 and 0.20 μ_B , respectively. Interestingly, the magnetic moment of adsorbed NO is always antiparallel with coordinated Ni irrespective of the surfaces magnetic phase; this will be discussed further later.

Upon NO adsorption, the hybridization between the NO 5s orbital and Ni $3d_{z^2}$ band in the bottom of the valence band decreases slightly (Figure 6(b)). Compared to the CO $2\pi^*$ orbital, which is completely unoccupied, the NO $2\pi^*$ orbital in the top of the valence band is partially occupied. For Ni($\uparrow$), it is mainly the Ni $3d_{x_{yz}}$ spin-down component populated in the top/upper part of the valence band. To maximize the hybridization between NO $2\pi^*$ and Ni $3d_{x_{yz}}$ in the top/upper part of the valence band, the occupied NO $2\pi^*$ must populate the spin-down component. In other words, the favorable configuration of magnetic moment between NO and coordinated Ni is antiparallel, namely, NO($\downarrow$) and coordinated Ni($\uparrow$), which is also found for NO adsorption on NiO(011).

Fig. 6. NO adsorption on AFM2(001). (a) Adsorption configuration; (b) SDOS of Ni 3d and NO 2p orbitals; (c) Isosurface view; (d) Section contour view of difference of electron density for NO adsorption. For isosurface view, yellow/green color means electron accumulation/depletion respectively.

Table 4

Magnetism and structure information of NO adsorption on NiO {001} surfaces. Magnetic moment (M_{Ni} , M_{NO}) is given in unit of μ_B . Adsorption energy of NO (E_{ads}) is given in eV. Bond length (d_{Ni-N}) is given in Å.

	$M_{Ni(clean)}(\uparrow)/\mu_B$	$M_{Ni}(\uparrow)/\mu_B$	$M_{NO}(\downarrow)/\mu_B$	$d_{Ni-N}/\text{Å}$	E_{ads}/eV
AFM1(001)	1.80	1.63	−0.61	2.00	−0.45
AFM1(100)	1.81	1.63	−0.61	2.00	−0.46
AFM2(001)	1.72	1.56	−0.58	2.05	−0.42
AFM3(001)	1.78	1.62	−0.63	2.01	−0.44
AFM3(100)	1.77	1.59	−0.60	1.98	−0.45
AFM4(001)	1.78	1.62	−0.62	2.00	−0.44
AFM4(100)	1.77	1.59	−0.57	1.98	−0.45
AFM5(001)	1.74	1.56	−0.61	1.98	−0.45
AFM5(100)	1.75	1.58	−0.58	1.99	−0.44
FM(001)	1.80	1.63	−0.56	1.99	−0.45

Regarding the decrease of the magnetic moment of adsorbed NO, we note that the peak intensity of NO $2\pi^*$ at the top of the valence band is smaller than those of the three other peaks of NO $2\pi^*$ in the conduction band. This indicates the electron depletion in the corresponding states (spin-down component), and accordingly, the NO magnetic moment decreases. Similarly, the decrease of the magnetic moment of coordinated Ni can be rationalized by the depletion of Ni $3d_{z^2}$ states (lower peak intensity) at the bottom of the valence band (spin-up component).

Compared to CO adsorption, the extra hybridization between NO $2\pi^*$ and Ni $3d_{x_{yz}}$ in the valence band strengthens the binding between NO and the coordinated Ni atom. The direct participation of the NO $2\pi^*$ orbital can be clearly seen from the difference of electron density plotted in Figure 6(c) and (d). Moreover, the magnitude of the difference of electron density induced by NO adsorption is about five times larger than that of CO (Figure 6(d) versus Figure 5(d)). The larger extent of electron redistribution induced by NO than by CO corroborates well with its stronger binding strength. For both CO adsorption (Figure 6(c) and (d)) and NO adsorption (Figure 5(c) and (d)), the adsorption-induced charge redistribution is limited to the singly coordinated Ni atom, and electrons of the NN Ni are hardly affected. In other words, the long-range magnetic phase has little influence on NO and CO adsorption on NiO(001).

3.3. NiO(011)

3.3.1. Surface properties

Without considering the magnetic phases, the {011} plane family consists of twelve equivalent planes. When taking into account the magnetism, the symmetry and degeneracy are broken. As listed in Table 5 and plotted schematically in Figure 7, for AFM1, AMF2, AFM3, and AFM4, there are two nonequivalent surfaces, and for AFM5, there are three inequivalent surfaces. This gives a total of eleven nonequivalent surfaces. For nonequivalent AFM1-(011), AFM2-(01 $\bar{1}$), AFM3-(110), and AFM5-(10 $\bar{1}$) surfaces, the local magnetic moments of the two adjacent surface Ni atoms are exclusively antiparallel ($\uparrow\downarrow$). Conversely, for nonequivalent AFM1-(110), AFM2-(011), AFM4-(110), and AFM5-(101) surfaces, the local magnetic

the conduction band (spin down), while $3d_{z^2}$, $3d_{xz}$, and $3d_{xy}$ are populated in the valence band. The upper part of the valence band originates largely from Ni $3d_{xy,xz}$ (spin down). Another prominent feature is the gap between the VBM and CBM of the Ni $3d$ band of 1.40 eV, which is much smaller than that of AFM2-(001) (2.81 eV) and AFM2 bulk (3.23 eV). The smaller $3d$ band gap of the surface Ni might facilitate its hybridization with adsorbed molecules, which will be discussed below.

3.3.2. CO adsorption

CO adsorption on these nonequivalent surfaces was studied, and the results at the most favorable sites are listed in Table 6. CO prefers to adsorb exclusively via the end of the C atom at the bridge site of two adjacent Ni atoms, labeled as A and B (Figure 9(a) and (c)). Irrespective of the nonequivalent surfaces and different bridge sites ($\uparrow\uparrow$ and $\uparrow\downarrow$) considered, CO has similar adsorption energies at the ($\uparrow\downarrow$) bridge sites (Figure 9(e)); the calculated adsorption energies vary from -0.73 to -0.75 eV. Conversely, for CO adsorption at the ($\uparrow\uparrow$) bridge sites (Figure 9(b)), the calculated adsorption energies are smaller (-0.71 to -0.72 eV). Thus, the local magnetic moment and its relative direction of two coordinated Ni atoms are responsible for the variation of the calculated adsorption energies rather than the long-range magnetic phases. The calculated binding strengths of CO on NiO {011} are about twice that of CO on NiO{001}, which possibly arises from the greater number of Ni–C bonds involved and the lower coordination number of surface Ni atoms.

Important geometrical parameters and the bond lengths between C and two coordinated Ni atoms are given in Table 6. The optimized C–Ni bond lengths are in the range of 2.13–2.23 Å, and longer than those of CO adsorbed on NiO(001) (2.02–2.07 Å). Irrespective of the magnetic phases considered, the C–O bond lengths stayed at a constant value of 1.15 Å,

Fig. 9. Adsorption of CO/NO on NiO AFM2(011) and AFM2(011̄). (a) AFM2(011) surface with bridge sites of Ni(A, $\uparrow$) and Ni(B, $\uparrow$); (b) CO and (c) NO adsorbed configuration on AFM2(011); (d) AFM2(011̄) surface with bridge sites of Ni(A, $\uparrow$) and Ni(B, $\downarrow$); (e) CO and (f) NO adsorbed configuration on AFM2(011̄).

which is 0.01 Å longer than that of gas-phase CO. CO adsorption has little influence on the surface magnetism: the magnetic moment for CO and coordinated Ni atoms decreased by only about 0.02 and 0.05 μ_B , respectively.

SDOS for CO adsorption at the ($\uparrow\uparrow$)-bridge sites of AFM2 NiO(011) are plotted in Figure 10(a). The magnetic moments of

Table 6

Magnetism and structure information of CO adsorption at the ($\uparrow\uparrow$)-bridge and ($\uparrow\downarrow$)-bridge sites of NiO {011} surfaces. Ni(A) always labels the Ni with total magnetic moment spin up. Magnetic moment (M_{Ni} , M_{CO}) is given in unit of μ_B . Bond length (d_{Ni-C}) is given in Å. Adsorption energy of CO (E_{ads}) is given in eV.

	$M_{Ni(clean)}/\mu_B$	$M_{Ni(A)}/\mu_B$	$M_{Ni(B)}/\mu_B$	M_{CO}/μ_B	$d_{Ni(A)-C}/\text{Å}$	$d_{Ni(B)-C}/\text{Å}$	E_{ads}/eV
($\uparrow\downarrow$)-bridge		($\uparrow$)	($\downarrow$)				
AFM1(011)	1.77	1.72	-1.72	0.01	2.13	2.15	-0.73
AFM2(011̄)	1.70	1.66	-1.66	0.00	2.18	2.18	-0.74
AFM3(011)X1	1.75	1.73	-1.73	0.04	2.19	2.16	-0.75
AFM3(110)	1.74	1.68	-1.68	0.00	2.13	2.13	-0.74
AFM4(011)X1	1.75	1.72	-1.72	-0.05	2.16	2.19	-0.72
AFM5(011)X1	1.72	1.67	-1.66	0.00	2.14	2.12	-0.74
AFM5(101̄)	1.72	1.67	-1.66	-0.01	2.14	2.12	-0.74
($\uparrow\uparrow$)-bridge		($\uparrow$)	($\uparrow$)				
AFM1(110)	1.78	1.74	1.74	0.02	2.17	2.17	-0.71
AFM2(011)	1.70	1.68	1.68	0.03	2.17	2.19	-0.71
AFM3(011)X2	1.75	1.72	1.72	0.05	2.18	2.19	-0.71
AFM4(011)X2	1.75	1.71	1.73	0.05	2.15	2.23	-0.71
AFM4(110)	1.74	1.69	1.69	0.00	2.15	2.14	-0.72
AFM5(011)X2	1.72	1.69	1.69	0.03	2.16	2.19	-0.71
AFM5(101)	1.73	1.70	1.70	0.06	2.18	2.17	-0.71
FM(011)	1.78	1.75	1.75	0.06	2.17	2.18	-0.71

Fig. 10. CO adsorption on AFM2(011) and AFM2(011̄). (a–c) CO adsorption on AFM2(011); (d–f) CO adsorption on AFM2(011̄); (a, d) SDOS for 3d orbitals of Ni(A) and Ni(B) labeled in Figure 9 and 2p orbitals of CO; (b, e) Isosurface view and (c, f) section contour view of spin-resolved difference of electron density for CO adsorption with spin-up component labeled UP and spin-down component labeled DOWN, respectively.

both Ni(A) and Ni(B) point upwards, which are denoted as Ni(A, ↑) and Ni(B, ↑), respectively. Figure 10(a) reveals that the spin-up components of Ni(A, ↑) and Ni(B, ↑) are nearly completely occupied. The hybridization occurs mainly via Ni(A, ↑)/Ni(B, ↑) back-donation towards CO. In contrast, the spin-down components of Ni(A, ↑) and Ni(B, ↑) are partially occupied, and hybridization occurs via CO donation to Ni(A, ↑)/Ni(B, ↑). Back donation in the spin-up component but donation in the spin down can be easily visualized in the spin-resolved difference of electron density results plotted in Figure 10(b) and (c). For the spin-up case, there is pronounced charge depletion from both Ni(A, ↑) and Ni(B, ↑) and accumulation in CO 2π* (back donation). For the spin-down component, there is charge depletion caused by CO 5σ donation and accumulation mainly between CO and Ni(A, ↑)/Ni(B, ↑).

SDOS for CO adsorption at the (↑↓) bridge sites of AFM2(011̄) are plotted in Figure 10(d), where the magnetic moments of Ni(A) and Ni(B) respectively point upwards (↑) and downwards (↓), and are denoted as Ni(A, ↑) and Ni(B, ↓), respectively. For the spin-up component, Ni(A, ↑) is nearly fully occupied and Ni(B, ↓) is partially occupied. Accordingly, the hybridization takes place via Ni(A, ↑) back donation toward CO, but CO donation toward Ni(B, ↓). This can be observed in the spin-resolved difference of electron density of the system (Figure 10(e) and (f)). There is modest charge depletion at Ni(A, ↑) for back donation and pronounced charge accumulation between CO and Ni(B, ↓) for CO donation. The relative larger extent of charge accumulation between CO and Ni(B, ↓) than that of charge depletion at Ni(A, ↑) indicates that donation rather than back donation plays a dominant role in the overall hybridization between CO and Ni. For the spin-down component

(Figure 10(d)), Ni(B, ↓) is nearly fully occupied and Ni(A, ↓) is partially occupied. Accordingly, the hybridization takes place via Ni(B, ↓) back donation toward CO and CO donation toward Ni(A, ↑). The distinct hybridization and charge redistribution for CO at the (↑↓) bridge sites from that of the (↑↑) bridge sites is in contrast to their similar adsorption energies (which differ by less than 0.03 eV).

3.3.3. NO adsorption

NO adsorption also occurs preferentially at the bridge site of two adjacent Ni atoms via the end of the N atom (Figure 9(c) and (f)). For all nonequivalent surfaces considered, the calculated adsorption energies for NO at the (↑↓) bridge sites are in the range of −0.99 to −1.05 eV and in the range of −1.21 to −1.30 eV at the (↑↑) bridge sites. Different from CO, the binding strengths at the (↑↑) bridge sites are about 0.3 eV stronger than those at the (↑↓) bridge sites. Moreover, the NO binding strength on NiO(011) is about three times stronger than that of NiO(001). For adsorption on (↑↑) or (↑↓) bridge sites, the difference of adsorption energy with variation of bulk magnetic order and surface index is less than 0.10 eV. In contrast, the variation of NO adsorption energy on all studied NiO(001) surfaces did not exceed 0.04 eV. This indicates that the larger variation of binding strength at all (↑↑) bridge sites (or (↑↓) bridge sites) of NiO(011) than that of NiO(001) may be simply caused by the higher surface activity of NiO(011). However, the difference of binding strength between adsorption at (↑↑) bridge sites and that at (↑↓) bridge sites of NiO(011) cannot be attributed to this reason. Again, the importance of the local magnetic order rather than the long-range magnetic phase is found here.

Important geometrical parameters for NO adsorption on NiO(011) are given in Table 7. Irrespective of the different magnetic phases considered, the N–O bond lengths stay constant at 1.19 Å, 0.02 Å longer than that of gas-phase NO. For NO adsorption at the ($\uparrow\uparrow$) bridge sites, the two N–Ni bond lengths are nearly same (1.96–1.97 Å). The corresponding NO magnetic moment prefers to align antiparallel with the two coordinated Ni($\uparrow$), namely, as NO($\downarrow$), as also found for NO adsorption on NiO(001). The magnetic moments of NO and coordinated Ni atoms decreased by at most 0.25 and 0.13 μ_B , respectively. For NO adsorption at the ($\uparrow\downarrow$) bridge sites, the two N–Ni bond lengths were not the same. The shorter one varied from 1.93 to 1.97 Å. The magnetic moments of NO and Ni corresponding to the shorter N–Ni bond pointed downwards ($\downarrow$) and upwards ($\uparrow$), decreasing by at most 0.43 and 0.20 μ_B , respectively. The longer N–Ni bond length varied from 2.03 to 2.09 Å, and there was little change of the magnetic moment of coordinated Ni($\downarrow$), which is understandable because of its relative longer N–Ni bond length.

Calculated SDOS for NO at the ($\uparrow\uparrow$) bridge sites of AFM2 NiO(011) is plotted in Figure 11(a), where the magnetic moments of both Ni(A) and Ni(B) point upwards and are denoted as Ni(A, $\uparrow$) and Ni(B, $\uparrow$), respectively. As noted above, the NO magnetic moment prefers to point downward ($\downarrow$); namely, there are more electrons occupied in the NO spin-down component than in the spin-up component. More electrons in the NO spin-down component would facilitate the corresponding donation process. This was verified in the spin-resolved difference of electron density results plotted in Figure 11(b) and (c), where charge accumulated between NO and coordinated Ni(A, $\uparrow$)/Ni(B, $\uparrow$). For the spin-up component, less electron occupation of the NO orbital would facilitate the corresponding back donation. This can be found in Figure 11(b) and (c), where charge depleted from coordinated Ni(A, $\uparrow$)/Ni(B, $\uparrow$) and accu-

mulated in the NO molecule.

Calculated SDOS for NO adsorbed at the ($\uparrow\downarrow$) bridge sites of AFM2(011) is plotted in Figure 11(d), where the magnetic moments of Ni(A) and Ni(B) point upwards and downwards and are denoted as Ni(A, $\uparrow$) and Ni(B, $\downarrow$), respectively. The N–O bond length with Ni(A, $\uparrow$) is shorter than that with Ni(B, $\downarrow$), and the NO magnetic moment points downward accordingly. The hybridization between NO($\downarrow$) and Ni(A, $\uparrow$) with antiparallel magnetic configuration is essentially the same as that for NO adsorption on AFM2(011) because the electronic and magnetic configurations are the same. This can be seen further in the corresponding difference of electron density plots (Figure 11(e) and (f)). Conversely, for NO($\downarrow$) and Ni(B, $\downarrow$) with same orientation of magnetic moments, the electronic hybridization between NO and Ni(B) is limited. Indeed, the difference of electron density (Figure 11(e) and (f)) between NO and Ni(B) becomes negligible, particularly in the spin-down component. This rationalizes well the weaker binding strength of NO adsorption at the ($\uparrow\downarrow$) bridge sites than that of NO at the ($\uparrow\uparrow$) bridge sites.

4. Conclusions

By constructing surface models of NiO with different magnetic phases, and using the paramagnetic molecule NO and nonparamagnetic molecule CO to probe the reactivity on (001) and (011) surfaces, we investigated the influence of magnetism on the surface chemistry of NiO. When the favorable adsorption sites involve only a single Ni cation, such as NO/CO adsorption at the top site of a Ni cation on the (001) surface, the long-range magnetic phases make little contribution to the overall adsorption behavior. The adsorption strength is primarily determined by chemical environment (such as surface orientation, coordination number, and adsorbed species). When the favorable

Table 7

Magnetism and structure information of NO adsorption at the ($\uparrow\uparrow$)-bridge and ($\uparrow\downarrow$) bridge sites of NiO {011} surfaces. Ni(A) always labels the Ni with total magnetic moment spin up. Magnetic moment (M_{Ni} , M_{NO}) is given in unit of μ_B . Bond length (d_{Ni-N}) is given in Å. Adsorption energy of NO (E_{ads}) is given in eV.

	$M_{Ni(clean)}/\mu_B$	$M_{Ni(A)}/\mu_B$	$M_{Ni(B)}/\mu_B$	M_{NO}/μ_B	$d_{Ni(A)-N}/\text{Å}$	$d_{Ni(B)-N}/\text{Å}$	E_{ads}/eV
($\uparrow\downarrow$)-bridge		($\uparrow$)	($\downarrow$)	($\downarrow$)			
AFM1(011)	1.77	1.58	−1.74	−0.47	1.93	2.03	−1.05
AFM2(011)	1.70	1.56	−1.71	−0.39	1.96	2.07	−1.01
AFM3(011)X1	1.75	1.54	−1.79	−0.64	1.95	2.08	−1.01
AFM3(110)	1.74	1.53	−1.78	−0.74	1.96	2.09	−1.05
AFM4(011)X1	1.75	1.57	−1.78	−0.65	1.97	2.05	−1.03
AFM5(011)X1	1.72	1.53	−1.75	−0.63	1.96	2.07	−1.02
AFM5(101)	1.72	1.54	−1.73	−0.30	1.94	2.05	−0.99
($\uparrow\uparrow$)-bridge		($\uparrow$)	($\uparrow$)	($\downarrow$)			
AFM1(110)	1.78	1.65	1.65	−0.68	1.97	1.97	−1.30
AFM2(011)	1.70	1.57	1.57	−0.61	1.97	1.97	−1.21
AFM3(011)X2	1.75	1.61	1.63	−0.49	1.96	1.97	−1.26
AFM4(011)X2	1.75	1.61	1.74	−0.47	1.96	1.97	−1.26
AFM4(110)	1.74	1.61	1.61	−0.72	1.96	1.96	−1.30
AFM5(011)X2	1.72	1.58	1.59	−0.53	1.96	1.97	−1.24
AFM5(101)	1.73	1.61	1.61	−0.53	1.97	1.97	−1.23
FM(011)	1.78	1.64	1.64	−0.59	1.96	1.96	−1.29

Fig. 11. NO adsorption on NiO AFM2(011) and AFM2(011̄). (a–c) NO adsorption on AFM2(011); (d–f) NO adsorption on AFM2(011̄); (a, d) SDOS for 3d orbitals of Ni(A) and Ni(B) labeled in Figure 9 and 2p orbitals of NO; (b, e) Isosurface view and (c, f) section contour view of spin-resolved charge flow diagram for NO adsorption with spin-up component labeled UP and spin-down component labeled DOWN, respectively.

adsorption site involves two adjacent Ni cations, such as NO/CO adsorption at the bridge site of two Ni cations in NiO(011), the local magnetic order of Ni ions coordinated to the adsorbed molecule rather than the long-range magnetism makes a considerable contribution to the overall adsorption behavior. For nonparamagnetic molecule CO, the orbital hybridization for adsorption at the ($\uparrow\uparrow$) bridge sites is very different from that at the ($\uparrow\downarrow$) bridge sites, despite their incidental similar adsorption energies. For paramagnetic molecule NO, the hybridization at the ($\uparrow\uparrow$) bridge sites is different from that at the ($\uparrow\downarrow$) bridge sites, and the binding strength of the former is about 0.3 eV stronger than that of the latter. The present work highlights the importance of the local magnetic order of TMO surfaces on molecule adsorption, particularly for paramagnetic molecules, at multi-fold sites.

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Graphical Abstract

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Influence of nickel(II) oxide surface magnetism on molecule adsorption: A first-principles study

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Calculations revealed that NO preferentially binds to Ni surfaces with its magnetic moment antiparallel to that of Ni. NO adsorbed at antiferromagnetic bridge sites binds to one Ni optimally and another in a frustrated manner.

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NiO表面磁性对分子吸附的影响的第一性原理研究

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摘要: 过渡金属氧化物广泛应用在当今能源与环境相关的催化领域, 理解其表面化学性质以及结构-反应活性之间的关系对于先进催化材料的进一步发展以至理性设计至关重要。3d后过渡系金属(Mn, Fe, Co, Ni)的氧化物以其中金属离子独特的自旋状态和由此产生的铁磁/反铁磁性为典型特征。研究过渡金属氧化物的自旋状态以及磁性对表面化学的影响将使我们更加完整了解这些材料的表面化学。以NiO为代表的后过渡系金属岩盐结构一元氧化物具有反铁磁性, 被经常作为反铁磁研究的模型体系。尽管在低温(低于其Neel温度)下NiO体相的完整晶体具有确定的反铁磁序, 但是一系列最新研究表明, 在条件变化时NiO表面的Ni离子可以产生不同的磁序。以此为背景, 本工作以NiO为模型体系, 采用DFT+U的第一性原理方法研究了NiO表面磁序对表面的小分子吸附活性的影响, 包括表面吸附活性对各磁性相的表面取向以及吸附物种磁性的依赖关系。我们考察了NiO的5种反铁磁相和一种铁磁相, 两个晶面NiO(001)和NiO(011), 顺磁性分子NO和非顺磁性分子

CO. 我们发现表面能受磁性的影响较轻微, NiO(001)面上从49到54 meV/Å², NiO(011)面上从162到172 meV/Å². 在NiO(001)面上, CO与NO都倾向于在Ni离子的顶位吸附. 对于不同的体相磁序与表面取向, CO吸附能的变化范围为−0.33 ~ −0.37 eV, NO吸附能的变化范围为−0.42 ~ −0.46 eV. 在NiO(011)表面, 两种分子都倾向于吸附在由两个Ni离子构成的桥位. 我们发现相对于NiO不同磁性相的体相长程磁序, 吸附位点处构成桥位的两个Ni离子的局部磁矩相对取向对于分子的吸附具有更加显著的影响. 计算得到NO在局部磁矩相对取向反平行(↑↓)吸附位点处的吸附能为−0.99 ~ −1.05 eV, 在局部磁矩相对取向平行(↑↑)吸附位点处吸附会增强, 吸附能为−1.21 ~ −1.30 eV. 对于CO, 尽管计算的吸附能在(↑↓)吸附位点(−0.73 ~ −0.75 eV)与在(↑↑)吸附位点(−0.71 ~ −0.72 eV)非常接近, 两种吸附位点处的CO吸附时分子轨道杂化方式以及吸附后CO的局域电子态密度却具有明显不同的特征. 本工作突出揭示了分子在过渡金属氧化物表面的多重吸附位点上吸附时吸附位点的局域磁矩相对取向对吸附性能的影响.

关键词: 磁性; 表面取向; 分子吸附; 第一性原理; 电子结构

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