Phenol near Ni(111), Ni(110), and Ni(221) surfaces in a vertical ring geometry: A density functional study of the oxygen-surface bonding and O-H cleavage

Luca M. Ghiringhelli, Riccarda Caputo, and Luigi Delle Site

Max-Planck-Institut für Polymerforschung, Postfach 3148, 55021 Mainz, Germany

Existing experimental studies of phenol on Ni(111) surfaces show no direct evidence for the formation of an oxygen-surface bond and O-H cleavage. Such processes are known for other transition metals [e.g., Pt(111) and Rh(111)] or other surface structures such as Ni(110). For this reason, we investigate the structure and energetics of a possible oxygen-surface bond and O-H cleavage for a phenol molecule interacting with a (close-packed) Ni(111) surface. In order to clarify the surface-molecule interaction, we make a comparison with different Ni surfaces, namely, the (110) and the (221)-step surfaces. By using a density functional theory approach, we find interesting agreement with experiments.

I. INTRODUCTION

Phenol adsorption on metal surfaces is a topic of high interest for its relevance in catalytic processes; despite its importance, only few *ab initio* studies are available.[1,2] Nowadays, due to the growing interest toward organic and/or inorganic interfaces, the relevance of phenol and/or metal interaction starts to expand beyond the scope of catalysis problems and to cover aspects related to different fields spanning from material science to biophysics and biotechnology. For example, such a system played the central role in modeling the adsorption of polymers, containing phenolic subunits, interacting with a metal surface.[2–5] As for benzene,[6–8] we have previously found[4] that phenol strongly interacts with the d electrons of the Ni(111) surface via its π orbitals. The maximum adsorption energy (i.e., the most stable configuration) was equal to −0.9 eV, with the center of mass located at the bridge site and the carbon ring lying flat on the surface. In Ref. 4, however, the attention was focused mainly on molecule-surface configurations which could mimic the adsorption of a phenolic chain end of polycarbonate on the surface; thus, that study did not require the analysis of bonds formed via the oxygen lone pairs nor of the possibility of O-H bond breaking. This latter aspect is actually particularly relevant for Ni(111); in fact, while for Rh(111) and Pt(111) experimental results clearly show that the phenol binds to the surface via the oxygen atom in a tilted or perpendicular geometry,[9,10] for Ni(111) there is no such evidence. In a particular experiment,[11] the interaction of phenol with the Ni(111) surface was studied with temperature-programed reaction, reflection-adsorption infrared spectroscopy (RAIS), and Auger electron spectroscopy. The RAIS technique was particularly useful in determining the correct bonding configuration; no signals in the RAIS spectrum corresponding to vibrations of the tilted ring were detected and this result led to the conclusion that the molecule must be bound with the ring parallel to the surface. Despite the high relevance of such a result, to our knowledge, there were no complementary theoretical studies which may support such conclusions. In Ref. 9, it was suggested that the mechanism of O-H cleavage should be as sketched in Fig. 1: first, the phenol forms a bond with the surface via the oxygen lone pair electrons, and subsequently, the O-H bond is broken. Our study is meant to

be complementary to our previous work,[4] which partially supports the experimental results of Ref. 11 regarding the parallel adsorption geometry via the π orbitals. In particular, we want to investigate in detail whether or not a bond between the surface and the oxygen can form and the bond breaking can occur via the mechanism suggested in Fig. 1. Since for the Ni(110) surface, there are experimental evidences of the O-H cleavage,[12] here we study also the adsorption and dissociation of phenol, again limited to the vertical ring orientation, onto the Ni(110) surface. Furthermore, in order to characterize the electronic properties of the molecule-metal bond, we include the study of the phenol adsorption onto a third surface, the Ni(221) step, as a representative of "open" metal surfaces.

II. COMPUTATIONAL DETAILS

We perform geometry optimizations using the pseudopotential based code CPMD (Ref. 13) in the free energy functional (FEMD) version.[14] In this method, the electron density and the Hellman-Feynman forces are determined via a subspace diagonalization of high-temperature electron-density matrix. We expanded the subspace in a plane-wave basis set with a cutoff of 60 Ry. Besides the adsorbing phenol, our systems consist of (a) a Ni(111) surface modeled using a (3×3) unit cell and four layers, (b) a Ni(110) surface represented by a (3×3) unit cell and four layers, and (c) a Ni(221) surface modeled as a (1×3) unit cell and three (111) layers. We employ a $3 \times 3 \times 1$, $2 \times 3 \times 1$, and $4 \times 4 \times 1$ k-point mesh in the Monkhorst-Pack scheme for the (111), (110), and (221) cases, respectively. The cell dimension in the z direction is 20 Å, which ensures that the thickness of the vacuum between the molecule and the bottom
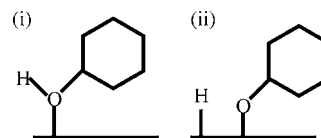

FIG. 1. Possible mechanism of adsorption for phenol on a transition metal. (i) A strong bond between the oxygen and the surface is formed; (ii) the O-H bond is broken and the hydrogen adsorbs.
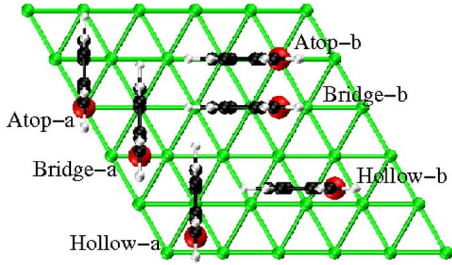
FIG. 2. (Color online) Top view of the the two main molecular orientations (in-plane orientations) in the plane of the Ni(111) surface with the oxygen (represented by the biggest sphere) located at each of the three high-symmetry sites.

layer of the image slab of nickel is at least 9–10 Å. We use a Troullier-Martins pseudopotential for oxygen and carbon,[15] a local one for hydrogen,[16] and the one developed by Lee for nickel.[17] The PBE generalized gradient approximation is applied.[18] The computational setup reported above was extensively tested in our previous work;[2–5,8] the maximum error on adsorption energies is estimated to be of 0.05 eV. During the optimizations, the bottom two layers of the surface were kept fixed for the (111) case, while all atomic coordinates were relaxed for the (110) and (221) cases.

III. RESULTS AND DISCUSSION

A. Ni(111) surface

Since we are interested in studying the possibility of a molecule-surface bond via the oxygen lone pairs and since the geometry with the carbonic ring parallel to the surface was already extensively studied in Ref. 4, here we look at vertical and tilted ring geometries (*out-of-plane* orientation) with the oxygen pointing to the surface. For both geometries, at each surface high-symmetry site, we consider the main molecular orientations in the plane parallel to the surface (*in-plane* orientation, i.e., the orientation of the projection of the carbon ring on a plane parallel to the surface, see Fig. 2). Each of these configurations was taken as initial input for a geometry optimization, and for each optimized structure, the

adsorption energy was calculated as $E_{ads}=E_{surface+phenol}-E_{surface}-E_{phenol}$, where all energies correspond to relaxed geometries. The whole structure was considered converged when the maximum component of the atomic forces fell below the value of 2×10^{-3} a.u. On the (111) surface, regardless of the initial in-plane molecular orientation and the location of the adsorption site, the tilted geometries tend to align parallel to the surface and eventually end up in configurations such as those found in Ref. 4. For the vertical geometries, no strong binding to the surface is found, the molecule stays vertical, and the most stable configuration corresponds (see Table I) to the oxygen located atop on a Ni atom, i.e., the configurations labeled as atop-a and atop-b in Fig. 2 (the difference of −0.04 eV in adsorption energy between them is negligible at our accuracy level). The atop nickel atom is lifted by 0.14 Å (atop-a) and 0.07 Å (atop-b) with respect to the average position of the top layer. The other four configurations either have nearly null adsorption energy (bridge-a and hollow-a) or are not bonding (bridge-b and hollow-b). The adsorption energy for the most stable configuration would not be high enough to justify the possibility of a mechanism such as that of Fig. 1, since a small thermal energy would be sufficient to tilt the molecule and drive it toward the flat high-energy configurations of Ref. 4. In order to check whether there is an energy barrier which hinders the phenol from finding a more adsorbing configuration with the oxygen closer to the surface, we studied the dependence of the adsorption energy on the distance of the oxygen from the surface. We started from the most stable configuration and adiabatically moved the molecule toward the surface. At each step, the z coordinate of the oxygen was kept fixed while the rest of the system was allowed to relax. The optimized geometry of each step was used as an input for the next step, with the molecule shifted by 0.1 Å toward the surface. The adsorption energy increases monotonically up to the nonbonding value of 0.16 eV; thus, no evidence for the existence of any barrier was found. A further check consisted in locating the molecule above the surface in such a way that the oxygen-surface distance was below 2.0 Å (characteristic O–metal bond distance, see, e.g., Ref. 19) and then allowing the system to relax without constraints; also, in this case, the system ends up in the minimum reported before. On

TABLE I. Adsorption energy (in eV) and structural data for the adsorption configurations of phenol (in its vertical ring orientation) onto the three Ni surfaces. The height of the oxygen atom above the surface (h_O) is calculated as $h_O=z_O-\bar{z}_{Ni}$, where z_O is the z coordinate of the O atom and $\bar{z}_{Ni}$ is the average z coordinate of the top layer of the Ni surface. The quantity d_{O-Ni} is the distance between the oxygen atom and the *closest* Ni atom. Both these distances are expressed in Å. The total number of displaced electrons Q and the squared charge displacement Q^2 are defined in text and are expressed in elementary charge (e) units.

Surface	Site	E_{ads}	h_O	d_{O-Ni}	Q	Q^2
(111)	Atop-a	−0.14	2.38	2.27	0.58	0.030
	Atop-b	−0.10	2.39	2.33		
(221)	Atop	−0.32	2.08	2.14	0.69	0.037
	Bridge	−0.26	2.11	2.29		
(110)	Atop	−0.35	2.16	2.14	0.75	0.041
	Bridge	−0.26	2.15	2.45		

the basis of such results, one can conclude that the O-H cleavage, as suggested in Fig. 1, is unlikely to happen. We further support this conclusion by additional calculations. First, we studied the effect of pulling away the hydroxy proton and let the system relax without constraints. We found that up to a stretch of about 60%–70% of the O-H equilibrium distance, the optimization returns to the initial configuration; only for a stretch larger than 70%, the bond is definitively broken and the hydrogen adsorbs onto the surface, but the barrier for this reaction is much higher than the small adsorption energy of phenol. In fact, by also doing an adiabatic stretch of 0.1 Å per step and fixing at each step the O-H distance with a 0.05 Å tolerance, we find a barrier for the dissociation of nearly 2.0 eV. On the basis of these results, we conclude that the interaction between phenol and the Ni(111) surface via the oxygen atom is so small that the O-H cleavage is unlikely to happen.

B. Ni(110) surface

The case of the Ni(110) surface is different. For this and the step surface, we did not optimize the system starting from all the possible configurations. Knowing that hydrogen, bonded in molecules to other atoms, is generally repelled by metal surfaces, we selected as initial configurations those that allow the molecule a certain freedom to keep the hydrogen as far as possible from the surface atoms. For the (110) surface, this criterion is matched by aligning the trace of the ring projected onto the (110) plane along the [001] direction, i.e., perpendicular to the "edge." We also find that in this case, the most adsorbing configuration is that of the atop, with $E_{ads}=-0.35$ eV, while the bridge site has a slightly lower value in magnitude (-0.26 eV). In the adsorption, the nickel surface undergoes a mild reconstruction, with the atop atom lifted by 0.06 Å from the layer average position; we also note that the atop atom in the third layer is lifted from the average position by 0.06 Å. From the equilibrium adsorbed configuration, we also studied the effect of pulling the hydrogen apart from the oxygen. In this case, we find a conformation with phenoxide still bound, via oxygen, at the atop site, while the hydrogen binds to the hollow site, with a total adsorption energy of the system of -0.25 eV; interestingly, we find the relatively small barrier of 0.7 eV for the O-H cleavage. This suggests that, in contrast with the (111) case, the cleavage is at least in competition with the desorption at finite temperature. The cleavage might be more favorable than that indicated by the values we find; in fact, the final state could be more stable than our -0.25 eV if hydrogen penetrates further into the open surface or binds to another dissociated hydrogen coming from a neighboring phenol molecule, to give molecular hydrogen. Furthermore, the simple way we estimated the barrier does not prevent the barrier from being lower than the value we find if more complicated mechanisms are available. We can conclude that, in sharp contrast with the (111) surface, for the (110) the dissociated state is *at worst* of comparable energy with the non-dissociated one, while the reaction barrier is *not higher than* 0.7 eV. This observation is consistent with the experimental findings of Ref. 12.
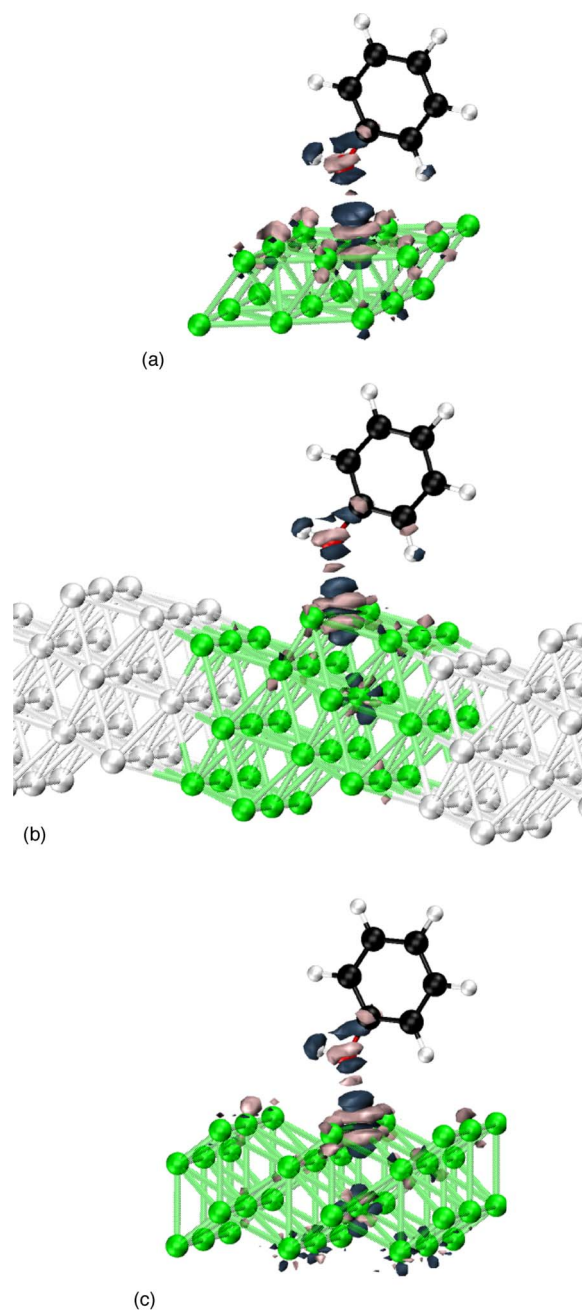

(a)

(b)

(c)

FIG. 3. (Color online) Electron-density displacement for the most adsorbing configuration of phenol onto a Ni (111) (top), (221)-step (center), and (110) (bottom) surface, for the vertical ring orientation. Only two of the four (111) planes used for the calculation are displayed. For the (110) and (221) cases, all the planes are displayed. For the (221) surface, only the metal atoms are periodically replicated to help visualize the step structure. The accumulation (depletion) zones are displayed by means of light (dark) colored isosurfaces at the level 0.02 $e/Å^3$.

C. Ni(221) surface

For the (221)-step surface, similarly to the (110) case, we studied only configurations with the trace of the phenol ring initially perpendicular to the step edge. We find the atop configuration to be the most adsorbing with $E_{ads}=-0.32$ eV, but the adsorption energy for the bridge site has the very

close value of −0.26 eV, i.e., at the limit of discrimination for our setup. Practically, the two adsorbing sites can be considered as equivalent. In the atop binding, the atop nickel atom is lifted by 0.05 Å with respect to the other two atoms constituting the unit edge.

D. Electronic properties

In Fig. 3, we show, for the most adsorbing configuration at each surface, the electron-density difference $\Delta\rho(\vec{r})$. This quantity is calculated by subtracting the electron densities of the isolated phenol and of the surface from the electron density of the adsorbed system. The O-Ni$_{atop}$ bond always has the same features on the three different surfaces. This is seen by looking at the space distribution of the accumulation and depletion electron-density zones in all the cases. The presence of a covalent bonding is marked by the accumulation region midway between oxygen and the atop nickel. Considering that the scales and the isosurface levels are exactly the same in the three panels, one can graphically note that the O-Ni bond is weaker on the (111) than on the other two surfaces. We also note that on the (111) surface, the polarization of the metal atom is largely confined to the six top layer neighbors of the atop atom, with a small fraction of polarization found around the three second layer neighbors of the atop atom. In contrast, for the (221) and (110), the polarization penetrates deep into the metal, suggesting a tighter binding with the metal layers. We define the number of transferred electrons as $Q=(1/2)\int d\vec{r}|\Delta\rho(\vec{r})|$, and the squared charge displacement as $Q^2=(1/2)\{\int d\vec{r}[\Delta\rho(\vec{r})]^2\}^{1/2}$. The latter quantity assigns more weight to the larger electron-density displacement, giving higher signature for more localized electron-density displacement. The calculated values for Q and Q^2 are in Table I. The trend of values for Q and Q^2 follows the magnitude of the adsorption energy; thus, the more bonded is the surface, the larger is the number of displaced electrons (Q) and the more localized (see Q^2) is the electron density.

E. Comparison to flat configurations

In vertical geometry, chemical intuition may suggest that phenol binds on the (111) surface via the formation of a relatively stable O-Me bond. We have shown that this is not the case for the (111) surface, but indeed it is the case for the more opened surfaces. The consequences are thus the following: on the (111) surface, "vertical ring" phenol indeed binds, via O-Ni bond, but the energy is small compared to thermal fluctuations. Thus, at any coverage, the only observable adsorption geometry would be the one studied in Ref. 4; this confirms the interpretation of the experiment reported in Ref. 9, which was still suffering from the lack of a theoretical counterpart. Our results lead to a further relevant point: on both the (110) and the step surface, the adsorption energy is strong compared to thermal fluctuations, while one may expect a much stronger bonding for the flat configuration also on these surfaces (see Ref. 6 for a rather similar molecule such as benzene). The vertical configuration might become competitive at high coverage, suggesting also the formation of a dense brush phase when phenol is a polymer chain end.

IV. CONCLUSIONS

We have presented a density functional study of the adsorption of phenol onto Ni(111), Ni(110), and Ni(221)-step surfaces, with phenol limited to its tilted and vertical ring orientations. This work is complementary to the study limited to the flat ring orientation presented in Ref. 4; here, we address the topic of the O-H cleavage after adsorption both on Ni(111) and Ni(110). Consistently with experimental observations, we find a mild adsorption ($E_{ads}=−0.14$ eV) of (vertical ring) phenol onto the atop site and an impracticably high barrier for the cleavage, and we find a stronger adsorption ($E_{ads}=−0.35$ eV) onto the Ni(110) surface and a relatively small activation barrier for the cleavage. On the (221)-step surface, we find an adsorption ($E_{ads}=−0.32$ eV) of strength practically equal to the (110) case. By means of electron-density displacement maps, we show a systematic comparison of the phenol bonding onto the three nickel surfaces, finding a clear trend of the covalent character of the bond that reflects on the trend in adsorption energies.

[1] S. D. Chakarova-Käck *et al.*, Phys. Rev. B **74**, 155402 (2006).

[2] L. Delle Site *et al.*, Phys. Rev. Lett. **89**, 156103 (2002).

[3] C. F. Abrams, L. Delle Site, and K. Kremer, Phys. Rev. E **67**, 021807 (2003).

[4] L. Delle Site, A. Alavi, and C. F. Abrams, Phys. Rev. B **67**, 193406 (2003).

[5] L. Delle Site, S. Leon, and K. Kremer, J. Am. Chem. Soc. **126**, 2944 (2003).

[6] F. Mittendorfer and J. Hafner, Surf. Sci. **472**, 133 (2001).

[7] S. Yamagishi, S. J. Jenkins, and D. A. King, J. Chem. Phys. **114**, 5765 (2001).

[8] L. Delle Site and D. Sebastiani, Phys. Rev. B **70**, 115401 (2004).

[9] X. Xu and C. M. Friend, J. Phys. Chem. **93**, 8072 (1989).

[10] H. Ihm and J. M. White, J. Phys. Chem. B **104**, 6202 (2000).

[11] A. K. Myers and J. B. Benziger, Langmuir **5**, 1270 (1989).

[12] D. Steinmüller, M. G. Ramsey, and F. P. Netzer, Surf. Sci. **271**, 567 (1992).

[13] J. Hutter, A. Alavi, T. Deutsch, and W. Silvestri, CPMD, version 3.4.1, MPI für Festkörperforschung and IBM Zurich Research Laboratory, 1995–1999.

[14] A. Alavi *et al.*, Phys. Rev. Lett. **73**, 2599 (1994).

[15] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[16] F. Gygi, Phys. Rev. B **48**, 11692 (1993).

[17] M. H. Lee, Ph.D. thesis, Cambridge University, 1995.

[18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[19] G. Wang *et al.*, J. Phys. Chem. B **109**, 12431 (2005).