

Effect of a step defect on the adsorption of benzene on the (221) surface of nickel: An *ab initio* study

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By employing an *ab initio* DFT approach we study the adsorption of benzene on a (221) step surface of nickel. We find an enhancement of about 0.3 eV for the maximum adsorption energy compared to that of the flat (111) surface. We perform an electron density analysis to characterize the nature of the molecule–surface bonds and compare it to the case of a flat (111) surface. We also find that the range of attraction in z direction is more extended than in the flat case; this result has important consequences in predicting adhesion properties of larger molecules, such as polymers at metal surfaces.

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I. INTRODUCTION

The interaction of benzene with transition metal surfaces is a subject of large interest for different fields; it is essential for understanding many catalytic processes and, more generally, phenylic adsorption determines the adhesion properties of larger molecules with aromatic groups. From polycarbonates to proteins, understanding adsorption mechanism at metal interfaces is a crucial key for both scientific and technological progress. The main goal of the study presented here is the modeling of the interaction between polymers and metal surfaces using efficient computational schemes. The interplay of computational approaches designed for different length scales and precisions, where parameters derived from quantum-mechanical calculations are plugged into meso- and macroscopic simulation models, is a subject of growing interest in the field of computer modeling. In our previous work^{1–5} we have focused on the development of a general multiscale modeling approach for simulating polymers interacting with (flat) metal surfaces. Within this approach, on the atomic scale, *ab initio* density functional methods were employed to describe the interaction of comonomeric subunits of bisphenol-a-polycarbonate (BPA-PC) with a nickel substrate. The resulting information was plugged into a coarse graining model to simulate the adsorption of long BPA-PC chains on a nickel surface. In the present work we study the mechanism of interaction of benzene with a (221) surface of nickel containing a step defect in view of applying the multiscale approach to imperfect surfaces; besides this primary goal our study aims at accurately describing and explaining fundamental properties of the molecule-surface adsorption. In particular we focus on the characterization of the difference between the step and flat case at a molecular level. In contrast to existing studies of the properties of steps in metallic surfaces^{6–8} we characterize the interaction of an aromatic π electron system with the particular electron distribution occurring at such a step. We investigate and quantify the reactivity of the two different surface topologies by determining the energy strength of their interaction with the aromatic molecule and by performing an electron density analysis to understand, at the electronic level, the nature of the molecule-surface bonding.

II. COMPUTATIONAL DETAILS

We use the FEMD code of Alavi^{9,10} implemented in the CPMD package.¹¹ In this method, with a self-consistent procedure, the electron density and the Hellmann-Feynman forces are computed using a subspace diagonalization of a high temperature electron density matrix. The subspace is expanded in a plane-wave basis setup to a cutoff of 60 Ry. A partial occupation of states at Fermi level can be handled and k -point sampling is also implemented. Apart from the adsorbed benzene molecule, our systems consist of a Ni(221) surface which is modeled using a (1×3) unit cell and three (111) layers (the distance between the step and its periodic image along the x -direction is $7.475\ 53\ \text{\AA}$), as well as a flat (111) surface modeled as a $p(3 \times 3)$ and four close-packed layers. We employ a $4 \times 4 \times 1$ k -point mesh in the Monkhorst-Pack scheme, the thickness of the vacuum between the benzene molecule and the bottom layer of the image slab of Ni(111) is always larger than $12\ \text{\AA}$. Troullier-Martins pseudopotentials were used for carbon,¹² a local pseudopotential is used for hydrogen¹³ and for nickel we chose the pseudopotential developed by Lee.¹⁴ We use the PBE¹⁵ generalized gradient approximation (GGA).

It is commonly assumed in literature,¹⁷ that spin polarization has only a minor effect on the adsorption energies and geometries of molecules on metallic surfaces. This holds even for magnetic materials such as nickel. As found by Yamagishi *et al.*,¹⁸ the application of the local spin density approximation (LSD) would not change the results significantly, while at least doubling the computational cost of the calculations.

Within this computational setup, we estimate the systematic numerical error for the total energy due to the various approximations to be of the order of 0.05 eV. We have also computed the interaction energy of the periodically repeated images of the benzene molecule by comparing to an isolated one calculated using the screening technique of Ref. 16. We obtain a repulsive value of 0.083 eV for the interaction energy in the configuration found for the step surface. Thus, any artifacts due to the finite covering of the surfaces are more than one order of magnitude smaller than the observed adhesion energies.

TABLE I. Adsorption energies of representative configurations at the step surface. Locations on the surface are schematically illustrated in Fig. 1. For comparison, the maximum adsorption energy in the flat case is also reported.

Position	E_{ad} (eV)
conf. (a)	1.37
conf. (d)	1.37
conf. (c)	1.05
conf. (e)	1.10
conf. (b)	0.7
conf. (f)	0.73
bridge _{flat-surface}	1.05

For the (111) flat surface our results were in satisfying agreement with those of previous calculations and experiments,¹⁷⁻¹⁹ while, the current work represents an attempt at a detailed understanding of the interaction between a benzene molecule and a step surface of nickel.

For the geometry optimizations, all atoms were free to relax to their equilibrium positions, no position constraints were applied. All structures were considered fully relaxed when the ionic forces fell below 2×10^{-3} atomic units. This convergence criterion represents the best achievable value at an affordable computational cost. A further optimization would have been prohibitively expensive, while its effect on actual adsorption energies would fall within the overall numerical noise of the calculation.

To check the effect of the finite thickness of the slabs, a fourth layer of nickel atoms was added to the step surface. The corresponding benzene adsorption energy in the energetically more favorable configuration was calculated, keeping the two bottom Ni-layers fixed. The effect of this additional layer could be shown to be about 0.1 eV for the adsorption energy.

III. RESULTS

Table I reports adsorption energies (E_{ad}) of six representative configurations at the step, depicted in Fig. 1, and, for comparison, the maximum adsorption energy we obtained for the flat case. The step surface is more reactive than the flat one. Four configurations exhibit equal or larger attraction strength than that of the flat case. Configurations (a) and (d) are those characterized by the highest interaction energy, for which, in comparison with the flat case, an enhancement of about 0.3 eV is found. Geometries (e) and (c) are characterized by values which are very close to that of the flat case. As a function of the lateral displacement of the benzene with respect to the step edge, the energy decays to a value of 0.73 eV for $\Delta x = 3.45$ Å. As in the flat case, hydrogens are rotated upward and carbon atoms form strong bonds with the nickel atoms at the surface. The energetically most stable configurations are not those where the center of mass of the carbon ring lies above the step edge, but those which have their center of mass shifted 1.0 Å, perpendicular to the step.

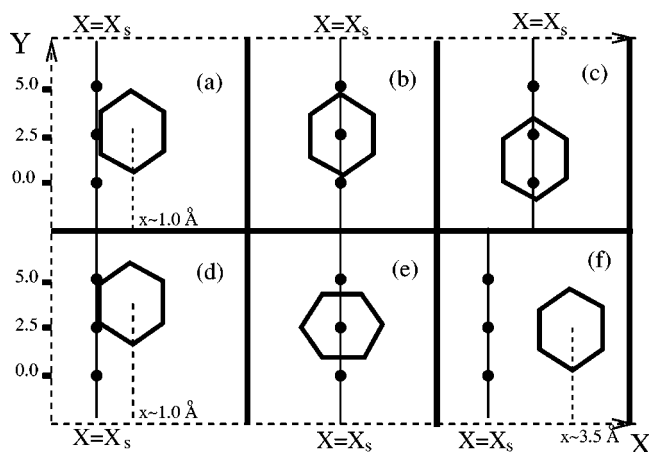


FIG. 1. Schematic plot, top view, of representative configurations of benzene on a Ni(221) surface. The x -axis indicates the direction perpendicular to the step edge ($X=X_s$) while the y -axis is parallel to it. The three black circles represent nickel atoms on the step edge and are in a 1:1 scale with the carbon ring.

In this latter case the carbon ring finds an optimal location for the creation of strong bonds²⁰ with several nickel atoms, while the number of available Ni bonding positions is smaller when the center of mass is above the step [cf. geometry (b) versus (d) in Fig. 2]. The two configurations in Figs. 2(b) and 5 exhibit the same adsorption energy although the bonding situations are very different. In the case of the flat surface (Fig. 5), each carbon atom forms a bond with a nickel atom while there are only two bonds in the step case. This result suggests that the higher reactivity of the step surface with benzene is due to its specific electronic properties rather than geometrically advantageous molecule-surface conformations.

In order to analyze this aspect, which represents the key for the interpretation of the difference between step and flat surfaces, we study the electron distribution of the two most stable configurations for the step and compare it with the flat case. We compute the difference in electronic density between the fragments (the nickel surface and the benzene molecule alone) and the chemisorbed system. For the fragments, we take the geometry found in the adsorbed state, in order to eliminate density variations due to backrelaxation of the atomic positions.

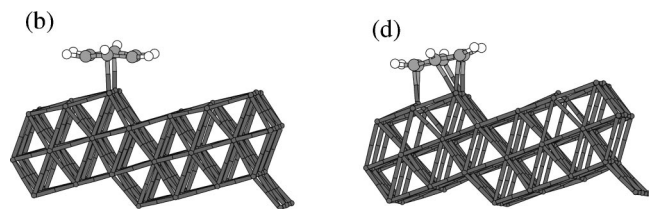


FIG. 2. Two optimized configurations at the step are shown, labels corresponding to those of Fig. 1: (b) the center of mass of the carbon ring lies above the step edge, and (d) with the center of mass shifted along the x -direction of about 1.0 Å. In the latter, carbon atoms can find a better location for forming strong C-Ni bonds.

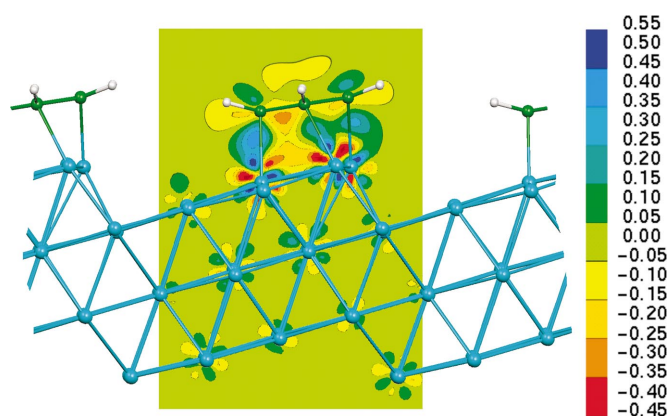


FIG. 3. (Color) Electronic density difference for the nickel-step surface for the conformation (a). The projection into the xz plane is shown. Yellow and red regions designate areas from which electronic density is taken away with respect to the isolated fragments, and green and blue colors mark regions to which it is transferred. Note the strong core polarization of the bonding Ni atoms, resulting in the creation of Ni-C bonds. The electronic density is also decreased in the aromatic regions below and above the benzene ring.

These calculations were done using the full k -point sampling of the Brillouin zone. The resulting plots representing the total density variation, integrated over the direction perpendicular to the cut, are shown in Figs. 3–5. For the step surface, we find a weak polarization of the electronic states within the slab, penetrating all three nickel layers. This effect is probably due to the finite size of the slabs.

Concerning the benzene molecule, we obtain a transfer of electronic density from the aromatic regions of the ring towards the assumed bonds with the nickel surface. Also the surface nickel atoms donate an important part of their electrons to the new bonds. The total integrated charge displacement due to adsorption, $1/2 \int d^3r |\rho_{\text{frag}} - \rho_{\text{ads}}|$, is about 2.15 elementary charges for conformation (a), 1.9 e for (d), and 2.1 e for the flat surface. Thus, the amount of transferred charge is very similar for all three situations. However, the visual impression from Figs. 3–5 is that polarization effects are stronger for the step configurations. To quantify this as-

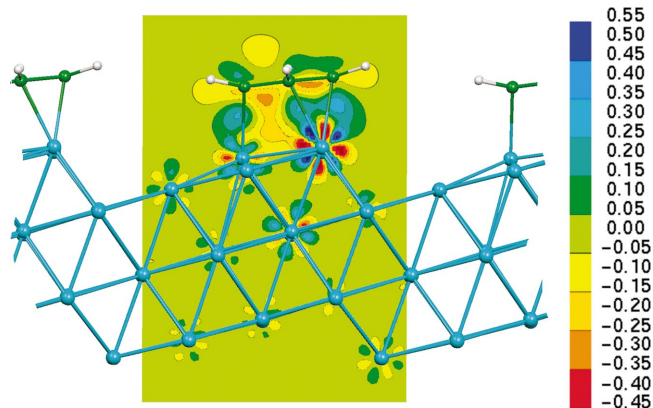


FIG. 4. (Color) Same as the previous figure for the configuration (d). The behavior is similar to that of the configuration of the previous figure.

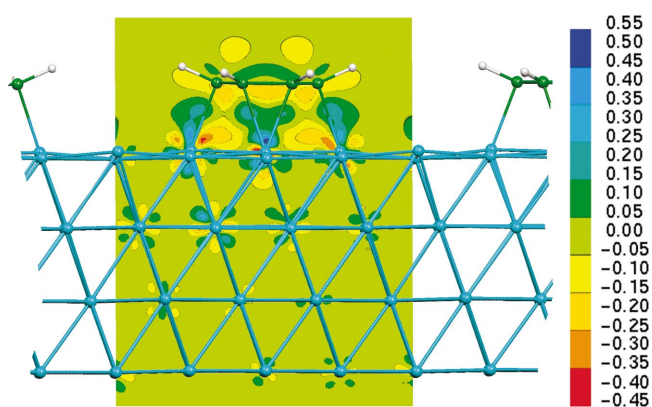


FIG. 5. (Color) Electronic density difference for the flat nickel surface projected onto the plane parallel to the paper.

pect, we have also computed the squared charge displacement, $1/2 (\int d^3r (\rho_{\text{frag}} - \rho_{\text{ads}})^2)^{1/2}$. This formula assigns more weight to larger charge differences. We obtain values of 0.11 e and 0.10 e for the step adsorptions, but only 0.085 e for the flat case. This indicates a more diffuse charge rearrangement of the latter, whereas the step defect is characterized by a somewhat sharper localization of the newly formed bonds.

In light of these results one can conclude that the specific electron distribution at the step plays the major role for the bonding process. Contrary to the fully symmetric flat case, the presence of an atomic irregularity such as a step induces a stronger polarization of the system. The larger charge transfer from the Ni atoms to the bonding region produces an enhancement of the adsorption energy for the step case. In comparison to the flat case, the step surface also exhibits a larger interaction range in z direction. For geometry (e), it decays to 0.5 eV at a distance of about 2.8 Å, which must be compared to 0.2 eV of the flat case. This difference is crucial for the interaction of BPA-PC with the surface; on the flat surface, adjacent submolecules are strongly repelled below a distance where the phenylene attraction is too weak to compete with the overall repulsion and as a consequence no adsorption is observed. For the step, there is less sterical hindrance from adjacent submolecules due to the topology of the surface and this, combined with the larger range of attraction in z direction, leads to adsorption of internal phenylenes at the step edge. Further calculations, to be submitted soon for publication,²¹ where these results are incorporated into the multiscale simulation scheme, show clear indications of localization of BPA-PC at the step edge.

IV. CONCLUSION

We have investigated the electronic origin of the adhesion mechanism of a benzene on a nickel surface, in particular the effect of a step defect. We have found, in agreement with the general behavior observed at a step defect on metal surfaces,^{6–8,22,23} that the step is more reactive than the flat surface. The adsorption energy at the step, in the optimal configuration, is enhanced by about 0.3 eV. We have also found that the strength of the interaction, as a function of the distance from the surface, decays less rapidly than in the flat

case. This result is of primary interest for the study of polycarbonates at a metal interface since, contrary to the case of a flat surface, the larger range of attraction allows internal phenylenes to bind to the surface providing a specific polymer-surface morphology at the interface. Different from the flat case, neither theoretical nor experimental results are available for the step. Considering the scientific and technological importance of this system, this lack of well founded data emphasizes the relevance of the current work and highlights the crucial need for experimental verification.

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