

Adsorption energies and geometries of phenol on the (111) surface of nickel: An *ab initio* studyL. Delle Site,¹ A. Alavi,² and C. F. Abrams^{1,*}¹Max-Planck-Institute for Polymer Research, P.O. Box 3148, D-55021 Mainz, Germany²Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

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The adsorption of a phenol molecule on a Ni(111) surface is studied by employing an *ab initio* DFT approach. Adsorption energies and geometries at each surface high symmetry site are determined and compared with the analogous case of benzene. Adsorption at the bridge site, with C-C bond along the $[\bar{2}11]$ direction, is found to be the most energetically favorable. Application of the current results to a multiscale modeling of polycarbonates interacting with a metal surface is briefly discussed.

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I. INTRODUCTION

The interest in studying the interaction of molecules with transition metal surfaces is usually associated with their catalytic activity. Certainly this is an important aspect, and benzene or benzenelike molecules, such as phenol, because of their high symmetry represent a convenient prototype of a relatively large molecule for such studies. At the same time, due to its high symmetry and to the fact that is a well understood system, Ni(111) represents a convenient model substrate. However, while it is possible to find several theoretical and experimental works for the benzene/Ni(111) system (see Refs. 1–3, and references therein), to our knowledge, the present work represents the first attempt at a detailed understanding of the interactions in the phenol/Ni(111) system.

The reason we performed this study is not directly related to possible consequences in catalysis but rather to the investigation at a multiscale level of the behavior of polymer molecules near metal surfaces. The idea of combining coarse-graining models for polymers with *ab initio* density functional theory (DFT) calculations for small molecule analogs of polymer subunits is particularly useful when polymers interact with interfaces where local chemistry may influence global properties of polymer systems. In particular, phenol (or benzene) can represent the chain-terminating phenoxy group of bisphenol A polycarbonate (BPA-PC). Its interaction with the surface can be extremely useful for understanding whether or not chain ends are attached to the surface, as we have shown using a multiscale approach in preceding work.^{4,5} Moreover, a better understanding of phenol behavior itself on a metal surface is warranted, due to its toxicity and widespread occurrence as a by-product. However, despite of an adsorption energy of about 1 eV (for both benzene and phenol) the adsorption of the *internal* benzene-like part of the BPA-PC chain (phenylene) is sterically forbidden due to the strong repulsion of the two neighboring submolecules in the chain. In fact, as we can anticipate, phenol (or benzene) presents a strong attraction in the optimal flat configuration at about 2.0 Å from the surface but its strength rapidly decreases as this distance increases. We have also shown⁵ that as the inclination of the carbon ring with respect to the surface increases the attraction rapidly decreases. These results combined with those about the adsorp-

tion of the other submolecules⁶ led to the conclusion that, while phenolic chain ends strongly adsorb on the surface, internal phenylenes are sterically hindered to adsorb. In fact, for example, at a distance of about 2.9 Å from the surface the *minimum* total repulsion energy of a monomer of the chain is about 0.18 eV (i.e., ≈ 3.6 kT, $T=570$ K to be compared with the typical thermal energy kT) and this quantity rapidly increases to ≈ 0.4 eV at 2.8 Å (≈ 8.0 kT) and to 0.7 eV (14.0 kT) at 2.6 Å.

II. TECHNICAL DETAILS

We use the DFT based finite-electronic temperature method of Alavi *et al.*^{7,8} (FEMD) implemented in the CPMD code.⁹ 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 density matrix. The subspace is expanded in a plane-wave basis set up to a cutoff of 60 Ry. A partial occupation of states at Fermi level can be handled and *k*-point sampling of the electronic states in the Brillouin zone of the supercell is also implemented. The system consists of a phenol molecule and a Ni(111) surface which is represented by four close-packed layers of Ni(111) (lattice parameter $a_0=3.543$ Å), with the top two layers (and the phenol molecule) allowed to relax. We use a (3×3) lateral supercell in hexagonal symmetry employing $3\times 3\times 1$ *k*-point mesh, the cell dimension in the *z* direction is 20 Å so that the thickness of the vacuum between the phenol molecule and the bottom layer of the image slab of Ni(111) is equal to about 12 Å. A Troullier-Martins pseudopotential is used for oxygen and carbon,¹⁰ a local pseudopotential is used for hydrogen¹¹ and for nickel the pseudopotential developed by Lee is used.¹² We use the PBE (Ref. 13) generalized gradient approximation (GGA). In order to check the validity of our setting, we performed a calculation for a benzene molecule at the bridge site of the Ni(111) surface, corresponding to the most energetically favorable configuration for such a system;^{1–3} our result for adsorption energy and geometry are in good agreement with previous work and experiments. We also tested our technical settings by performing calculations for bulk nickel, surface, and phenol isolated molecule; structural parameters and energies were reproduced in good agreement with previous work and experiments.^{14–16}

TABLE I. Adsorption energies at high symmetry sites for phenol and benzene. For benzene the data were taken from Ref. 1; for bridge A we report also the result of our calculation. Because of the higher symmetry of the benzene with respect to the phenol, configurations type 1 and type 2 coincide for benzene.

| Position | E_{ad} (eV) phenol | E_{ad} (eV) benzene |
|----------|----------------------|-----------------------|
| fccA1 | 0.73 | 0.78 |
| fccA2 | 0.79 | 0.78 |
| fccB | 0.67 | 0.94 |
| hcpA1 | 0.75 | 0.84 |
| hcpA2 | 0.84 | 0.84 |
| hcpB | 0.73 | 0.91 |
| AtopB | 0.20 | 0.42 |
| AtopA | 0.02 | |
| BridgeB1 | 0.74 | 0.74 |
| BridgeB2 | 0.64 | 0.74 |
| BridgeA1 | 0.86 | 1.00/(1.05 our value) |
| BridgeA2 | 0.91 | 1.00/(1.05 our value) |

III. ENERGY AND GEOMETRY OF ADSORBED PHENOL AT THE SURFACE HIGH SYMMETRY SITES

Table I shows the adsorption energy for each possible molecular orientation on the plane parallel to the surface at each high symmetry site of the surface (see Fig. 1). This is compared with the corresponding value for benzene. For the phenol the substitution of a H with an O-H reduces the symmetry of the molecule with respect to the benzene, and for this reason the number of possible symmetric geometries at each different high symmetry site increases as will be speci-

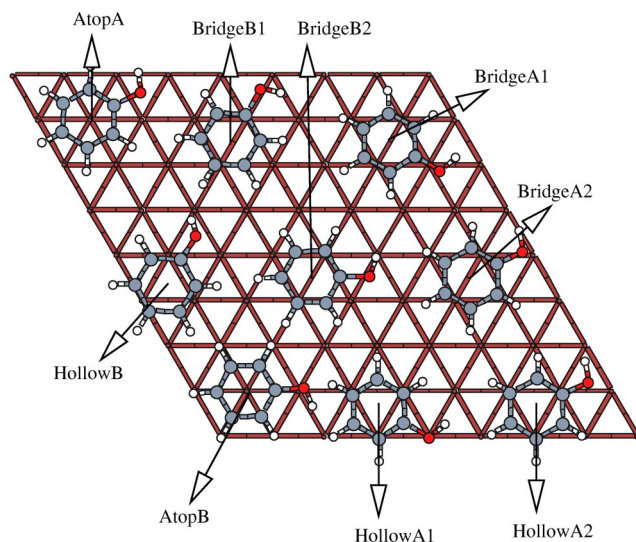


FIG. 1. Possible orientations of phenol at the four high symmetry sites of the (111) nickel surface. Letters A,B specify the carbon ring orientation while numbers 1,2 specify, for a given ring orientation, the O-H position with respect to the surface. Here for simplicity only the top layer is illustrated (we used four layers), one should read the hollow configurations as hollow hcp type and fcc type.

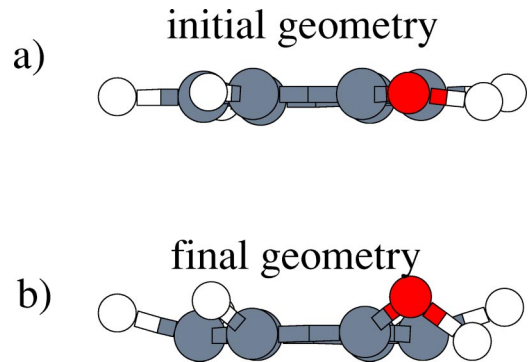


FIG. 2. The figure compares the optimized configuration of the isolated phenol (a), with a phenol configuration taken from an optimized Ni/phenol system (b). The most evident features is the upward rotation of the oxygen, which probably makes the Ni-C bonds weaker.

fied next; this, as one can expect, will play the major role in determining the properties of the bond between molecule and surface.

The orientation of the carbon ring on the plane parallel to the surface is indicated by the letters A and B, while numbers 1 and 2 indicate the possible location of the O-H with respect to the atoms of the surface. In all the cases considered the carbonic ring lies parallel to the surface at an average distance of about 2.0 Å, this because having calculated the energy as a function of the inclination with respect to the plane of the surface we found that the energy rapidly decays as the inclination increases (reduced to 0.05 eV beyond 40° which must be compared with 0.9 eV for the optimal parallel configuration). The fixed point of the rotation is a hydrogen attached to a carbon, this choice was taken because the molecular orientation should be consistent with the polymer topological constraints. The same was done as function of the distance from the surface and found that also in this case the interaction rapidly decays (reduced to 0.03 eV beyond 3.0 Å). As one can see from Table I, for each site the adsorption energy is always less or equal than the corresponding for benzene; considering the precision of the calculation and the fact that the phenol has a lower coverage, the systematic difference is within 0.1 eV. These results in general mean that the presence of the oxygen, by rotating upward, as illustrated in Fig. 2, makes one of the C-Ni bonds weaker; this seems to be the main characteristic of the molecule-surface interaction.

One can also note that for the same position over the surface, the energy can be significantly different depending on the O-H location in the ring. For example for hcpA2 and hcpA1, the difference is due to the fact that in the first case the projection of the oxygen on the surface lies at the center of the equilateral triangle formed by 3 Ni atoms, while in the second case is on a Ni atom of the surface. This fact suggests that there exists a weaker repulsion in the first case compared to the second. As for benzene, bridge A2 (bridge A1), i.e., bridge site with C-C bond along the $[\bar{2}11]$ direction, turns out to be the energetically most favorable position for phenol. The weaker bonding energy is probably due to the fact that the carbon attached to the O-H has a larger bonding

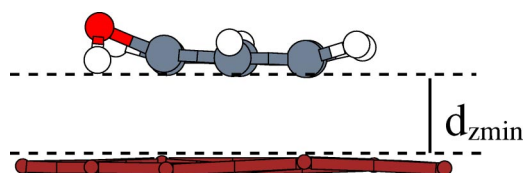


FIG. 3. The figure shows the top layer of the Ni surface and the phenol molecule lying over the atop site in configuration B (atopB). The meaning of $d_{z\min}$, i.e., the minimum distance along the z coordinate between the phenol and the top layer is graphically illustrated.

distance from the Ni atom with respect to the corresponding C in benzene. Also, in general the average C-Ni bonding distance is larger for phenol than benzene.

As for benzene, the carbon ring is uniformly expanded with respect to the isolated phenol, being characterized by a larger C-C bond length, and, in the case of phenol, the expansion is slightly smaller than the benzene. The average length of the C-H bonds remains constant, within an error of less than 0.5%, with respect to the isolated phenol, but an upward rotation with respect to the carbon ring can be noticed, exactly as in the benzene case. As anticipated above, significant upward rotation of the oxygen is also seen. In general, the number of bonds between the C atoms and the Ni atoms (defined as a distance less than or equal to the average carbon metal bond 2.14 Å) is smaller for phenol; moreover the C-Ni average distance and the $d_{z\min}$ as well as \bar{d}_z (i.e., distances molecule-surface perpendicular to the surface; see Figs. 3 and 4) are larger for phenol, this clearly leads to a weaker interaction, making the C-Ni bond weaker in general. The upward shift of some Ni atoms is significantly larger than the inward shift of some other Ni atoms,

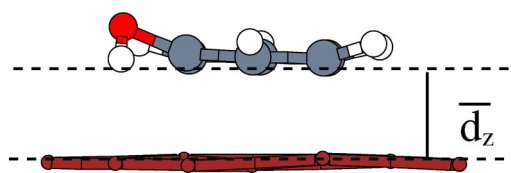


FIG. 4. The figure shows the top layer of the Ni surface and the phenol molecule lying over the atop site in configuration B (atopB). The meaning of \bar{d}_z , i.e., the average distance along the z direction is graphically illustrated.

for both first and second layer; this is due to the C-Ni bonds on the surface, while the inward shift is probably due to lateral compressive stress.

IV. CONCLUSION

We analyzed the adsorption process of a phenol molecule on each high symmetry site of a Ni(111) surface. We found that the adsorption at the bridge site, with C-C bond along the $[\bar{2}11]$ direction, which we termed bridge A2, is energetically the most favorable, while in general adsorption at the atop site is the less favorable. Comparison has also been made with the adsorption of benzene, where experimental data are available. The main result to emerge from this study is that the phenol molecule-surface interaction with Ni(111) is reduced compared to that of benzene. The results presented are important not only for a better understanding of molecule-nickel interaction process but also in building a multiscale model for the interaction of polycarbonates, containing phenol (benzene)-like submolecules as component of the chain, with a metal surface. We have elsewhere applied this strategy for the example of BPA-PC on a (111) nickel surface.^{4,5}

*Current address: Department of Chemical Engineering, Drexel University, Philadelphia, PA 19104.

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