



Hydrazine network on Cu(111) surface: A Density Functional Theory approach



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ABSTRACT

We have used first-principles calculations, including a correction for the dispersive forces (DFT-D2), to investigate the arrangement of hydrazine (N_2H_4) molecules upon adsorption on the Cu(111) surface, showing that surface–molecule interactions affect the process most. Our calculations provide insight into the interplay between lateral adsorbate–adsorbate and vertical adsorbate–substrate interactions. We found that the main contributors to the assembly of the hydrazine layers are the binding interactions between the adsorbates and the substrate. The dispersion forces are predominant in both vertical and lateral interactions, whereas hydrogen-bonding is least important and organisation of the N_2H_4 monolayers is therefore primarily due to the long-range interactions. Optimised geometries for several hydrazine conformations were found to be coverage-dependent. The electronic properties such as charge density and density of states have been calculated for different hydrazine coverages, and indicated that no charge transfer occurs between molecules. Scanning tunnelling microscopy images were simulated, where the observed protrusions arise from the trans conformers. We also found that the effect of hydrazine adsorption on the Cu(111) surface energy is negligible and further investigation of other Cu facets is needed to determine the N_2H_4 effect on the nanoparticles' morphology. Finally, we have simulated the temperature programmed desorption of different coverages of hydrazine from the Cu(111) resulting in desorption peaks between 150 and 200 K.

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1. Introduction

The assembly of organic molecules on solid surfaces is finding increasing applications in nanoscience, due to the ease of preparation and their power to control surface chemical and physical properties. The driving forces that induce the formation of highly ordered assembled molecular structures on the substrate are the adsorbate–adsorbate and adsorbate–substrate interactions. The molecular orientation during the assembly process may be governed by long-range binding forces such as hydrogen-bonding, dipole–dipole, van der Waals (vdW) and electrostatic interactions which act at a molecular level. Owing to the directional nature of these interactions, especially hydrogen-bonding, they may be used as control tools in the design of assembled monolayers [1]. A fundamental understanding of these interactions will help to better control the structure and properties of these systems [2]. Density Functional Theory (DFT) is a suitable technique to investigate the assembly process at the atomic level and the electronic structures of the systems at different coverages of molecules, as successfully shown on a number of substrates [3–8].

Molecular assembly of adsorbates may also be applied in the synthesis of well-defined nanoparticles for specific applications. Understanding the nanoparticle production process helps us to generate particles with specific sizes, morphologies and desired properties for particular applications. Reverse micelle-based synthesis, for instance, has achieved much in the way of controlling the size and shape of copper nanoparticles, although the underlying processes are still not fully understood. Many factors affect the size and shape of nanoparticles and one important factor is the concentration of the reducing–capping agent, e.g. hydrazine (N_2H_4), which experiment has shown has a strong effect on the nanoparticle morphology [9–15]. Thus, understanding the molecular adsorption of N_2H_4 on the dominant Cu(111) surface at different coverages may help identify measures to control the growth direction and design of copper and other metal nanoparticles.

In this paper we have applied electronic structure calculations based on the Density Functional Theory (DFT), with additional semi-empirical terms to take into account essential dispersion interactions, to investigate the interactions between hydrazine molecules. We have investigated the systems with different concentrations of hydrazine, forming a network layer at the molecular level, to provide insight into the interplay between lateral adsorbate–adsorbate and vertical

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adsorbate–substrate interactions, and to deduce the effect of the concentration of hydrazine on the copper crystal shape. The application of a full monolayer allows us to mimic the hydrazine assembly and understand the intermolecular interactions. We have also modelled scanning tunnelling microscopy (STM) images for future comparison with experiment.

2. Computational methods

In this study we have employed the Vienna Ab-initio Simulation Package (VASP) [16,17], which allows calculations based on the Density Functional Theory (DFT) [16–19] using pseudopotentials and plane-wave basis sets. The Perdew, Burke and Ernzerhof (PBE) [20] form of the GGA pseudopotentials [21,22] is used here for calculations within the general gradient approximation, to carry out our total energy calculations and perform geometry optimisations by minimizing the forces and stress tensor on the systems. Only the valence electrons were treated explicitly and their interactions with the ionic cores were described by the Projector Augmented-Wave (PAW) method [22]. The cut-off energy for the expansion of the plane-wave basis sets was set at 600 eV, which gave bulk energies converged to within 0.001 eV/atom. To improve the description of the long-range interactions, we have employed the DFT-D2 [23,24] method of Grimme as implemented in VASP, which has been shown to make important contributions to the surface–molecule interactions [3,25–27]. In this approach the total energy is calculated as a function of the dispersion coefficient for each atom pair, a global scaling factor that depends only on the exchange–correlation functional used, which is 0.75 for the PBE functional, and a damping function to avoid near singularities for small distances. The integration of the Brillouin zone was done using the Monkhorst–Pack [28] $11 \times 11 \times 11$ and $3 \times 3 \times 1$ k-point grids for the bulk and surface simulations, respectively.

Following our previous work [25,26], we have used a slab model of four atomic layers, in which the three uppermost layers were free to relax during the optimization, while the bottom layer was kept frozen at the optimised bulk positions. This set-up, where one side of the slab is kept fixed, ensures the explicit geometry optimisation of a realistic number of surface layers, while still retaining a reasonably sized slab which made it feasible to investigate a large number of initial adsorption geometries. To evaluate the model, structural relaxations of the clean Cu(111) surfaces were performed as a measure of the accuracy of the surface structure. They are calculated as the percentage relaxations of the atomic layers using Eq. (1):

$$\Delta d_{ij} \% = \left[(d_{ij} - d_{bulk}) / d_{bulk} \right] \times 100 \quad (1)$$

where d_{ij} is the interlayer distance in the relaxed surface and d_{bulk} is the bulk layer spacing, which is given by the spacing of the fixed layers in the slab. The results for a 4-layer slab with different numbers of relaxed layers are summarised in Table 1, where minus signs correspond to contraction. We note a contraction (–0.12%) in the first interlayer relaxation of the Cu(111) surface with three relaxed layers, in good agreement with experiment. Furthermore, the second interlayer exhibits an even larger contraction (–0.40%), while the interlayer spacing d_{34} (–0.04%) remains almost unchanged.

We have also calculated the relaxed surface energies for the clean Cu(111) with different numbers of relaxed layers, where the unrelaxed surface energy (γ_u) is calculated as follows, Eq. (2):

$$\gamma_u = \frac{E_{slab,u} - nE_{bulk}}{2A} \quad (2)$$

$E_{slab,u}$ is the energy of the unrelaxed slab, E_{bulk} is the energy of the primitive cell, n is the number of atoms in the slab compared with the ones in the bulk and A is the surface area of one side of the slab. We have then calculated the relaxed surface energy (γ_r) using Eq. (3); where $E_{slab,r}$ is the energy of the relaxed slab with one side fixed in the optimised bulk geometry.

$$\gamma_r = \frac{E_{slab,r} - nE_{bulk}}{A} - \gamma_u \quad (3)$$

Table 1 presents the relaxed surface energies for a 4-layer slab with different numbers of relaxed layers, which shows that the surface energies converge very well with respect to the number of relaxed layers for the Cu(111) surface.

The slab used is a 3×3 supercell from the full unit cell, $p(6 \times 6)$, containing 36 atoms per layer (144 Cu atoms/unit cell) and exposing an area of 198.8 \AA^2 , which enables us to investigate a realistic hydrazine network. A vacuum of 20 \AA was included between the slabs to avoid perpendicular interactions between images. We have also employed a perpendicular dipole correction to enhance energy convergence of the adsorbed systems. The geometry of the hydrazine molecule was optimised in the gas phase using a cubic box of $20 \times 20 \times 20 \text{ \AA}^3$, where the relaxed gauche conformer was found to be the most stable structure, being lower in energy by 0.13 eV relative to the trans and by 0.36 eV relative to the eclipsed conformation.

We started building an overlayer of hydrazine molecules from a single hydrazine on the Cu(111), as investigated previously [25], and increasing to two, three, four, five, six and nine molecules per cell, resulting in a wide range of coverages: from 0.50 to 4.53 molecules/nm². We carried out a relaxation of the geometry after each addition.

The adsorption energy (E_{ads}) per molecule was calculated as the difference between the total energy of the optimised substrate–adsorbate system ($E_{slab+n mol}$) and the sum of the energy of the relaxed clean surface (E_{slab}) and n times the energy of an isolated N_2H_4 (E_{mol}) in the gauche conformation, which is the most stable hydrazine conformer in the gas phase; n is the number of hydrazine molecules, Eq. (4):

$$E_{ads} = [E_{slab+n mol} - (E_{slab} + n \cdot E_{mol})] / n \quad (4)$$

The binding and cohesion energies per molecule have also been calculated to discuss the interplay between transversal (E_{bind}) and lateral interactions (E_{cohe}) [32], which are defined as

$$E_{bind} = [E_{slab+n mol} - (E_{slab}^* + nE_{nmol})] / n \quad (5)$$

$$E_{cohe} = [E_{nmol} - nE_{mol}] / n \quad (6)$$

where, E_{nmol} is the energy of the hydrazine network in the vacuum and E_{slab}^* is the energy of the copper surface, both with the same geometry as found in the adsorbate–substrate calculation (denoted by the asterisk). Within this definition, negative E_{ads} , E_{bind} and E_{cohe} values mean a

Table 1
The relaxed surface energies γ and percentage interlayer relaxation of clean Cu(111) slabs with different numbers of relaxed layers.

	Bulk	1 relaxed layer	2 relaxed layers	3 relaxed layers	Exp
γ (J/m ²)	1.9714	1.9712	1.9696	1.9695	2.02 [29]
Δd_{12} (%)	–	–0.08	–0.08	–0.12	–0.7 ± 0.5 [30], –0.3 ± 1.0 [31]
Δd_{23} (%)	–	–	–0.44	–0.40	–
Δd_{34} (%)	–	–	–	–0.04	–

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