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Ab initio DFT studies of adsorption characteristics of benzene on close-packed surfaces of transition metals

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ABSTRACT

We investigate the adsorption of benzene on close-packed surfaces like the (1 1 1) surface of fcc, the (1 1 0) surface of bcc and the (0 0 0 1) surface of hcp transition metals, using plane wave DFT calculations. The bridge site is the most stable adsorption site for all (1 1 1) surfaces, except in case of Rh, Ru where the hollow site is found to be most stable and for Mo, W where an intermediate position between bridge and hollow is preferred. Comparing with experimental measurements wherever available shows that van der Waals (vdW) interaction are significant in determining the adsorption energy accurately. Changes in geometry and electronic structure after adsorption are studied. It is found that in case of transition metals having partially filled *d* bands, a net electron transfer takes place, towards the benzene molecule and for metals having filled or nearly filled *d* band (Pt, Pd) the net transfer is towards the substrate.

1. Introduction

The interaction of aromatic molecules with transition metal surfaces is an important field of study, having a wide range of applications ranging from heterogeneous catalysis, petroleum refining, polymer production to molecular electronics and spintronics [1–3]. Benzene, which is theoretically the simplest and smallest aromatic molecule, is used as a model adsorbate in our study. Benzene is industrially important as a precursor to synthesis of many other organic molecules. The conversion of benzene to cyclohexane through hydrogenation is an industrially important process [4]. Usually hydrogenation is performed in the presence of transition metals or alloys that act as catalyst. The metal-benzene interface thus plays an important role in catalysis. The benzene molecule is bound to the metal surface either by physisorption or chemisorption forces. It is understood that in physisorption the dispersive van der Waals (vdW) forces play an important role, while in the case of chemisorption, the molecule forms a chemical bond with the surface. Transition metal surfaces may be broadly classified into two groups based on this interaction, one which includes reactive metals like Pt, Pd, Rh, Ir, Ru, and ferromagnetic materials like Ni, Co, and Fe over which benzene is chemisorbed, and the other which includes coinage metals like Cu, Ag, and Au over which benzene is merely physisorbed.

The adsorption of benzene on transition metal surfaces has been fairly intensely studied, both experimentally and theoretically over last several years. Adsorption energy is one of the key parameter that determines the strength of interaction. There may be several possible sites and orientation of the adsorbate on the surface, of varying symmetry, of which a preferred site or orientation for each molecule can be experimentally identified. Experimental techniques to measure adsorption energies include Reflection Absorption IR Spectroscopy (RAIRS) [5], Scanning Tunneling Microscopy (STM) [6–8], Temperature Programmed Desorption (TPD) [9–11], Electron Energy Loss Spectroscopy (EELS) [12–14], Near Edge X-ray Adsorption Fine Structure (NEXAFS) [15–17], Low Energy Electron Diffraction (LEED) [18–20,11], and Angle Resolved Ultra Violet Photo Electron Spectroscopy (ARUPS) [21,22]. Microcalorimetry measurements are mainly used to determine the heat released during adsorption process [23,24]. An accurate measurement of heat released during the adsorption of benzene on Pt (1 1 1) was recently measured by Campbell's group using Single Crystal Adsorption Calorimetry (SCAC) [25,26]. The information from these different experimental studies on preferred adsorption site and adsorption energy is often found contradicting and hard to interpret, which makes the theoretical studies more important.

The density functional theory (DFT) is the most popular theoretical technique used to describe the adsorption process. However

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there exist also, several ab initio Molecular Dynamics (MD) calculations for adsorption of small molecules on metal surfaces, which allows to include explicitly the temperature effects into the calculations [27,28]. Studies on adsorption of benzene on (1 1 1) surfaces of reactive metals like Pt, Pd, Rh [29–31] and also on coinage metals like Ag, Au, Cu [32,33], employing different versions of GGA functionals like PBE and PW91 are reported. The adsorption energy obtained from these studies was significantly different compared to experimentally measured values obtained from the TPD and microcalorimetry measurements. It was reasoned that GGA functionals fails to include long range dispersive van der Waals (vdW) forces, which are important in describing sparse matter systems, especially surface adsorption and related phenomena [34]. Recent improvements in the DFT exchange correlation functional to include van der Waals (vdW) interaction has led to computing of adsorption energies with much greater accuracy. To account for vdW interaction, there are several approaches, which are described and classified by Klimes and Michaelides in their review on dispersion forces in DFT as a hierarchical scheme of corrections, each with increasing accuracy and cost of computation [35]. The lowest step of this "stairway" starts with a pair-wise electronic energy term that accounts for long range interaction added to the DFT total energy. The approach termed as DFT-D method uses constant dispersion coefficients and neglects any variation in these with the environment of the atoms [36]. At the next level, several methods are available such as Grimme's DFT-D3 [37], Tkatchenko and Scheffler vdW (TS) [38] and the Becke-Johnson model (BJ) [39]. All these methods involve environment dependent coefficients (designated as C_6 coefficients) to calculate the dispersion energy. These methods require pre-determined external inputs and therefore are not truly ab initio in sprit. The van der Waals density functionals (vdW-DF) are placed on the third step of the stairway [40,41,42–44] and is a true functional of the electron density. In this method proposed by Dion et al. [44], the exchange-correlation energy may be expressed as

$$E_{xc} = E_x^{GGA} + E_c^{LDA} + E_c^{nl} \tag{1}$$

where E_x^{GGA} is the exchange energy, E_c^{LDA} is the LDA correlation energy and E_c^{nl} is a density dependent non-local correlation energy term. The original vdW-DF uses revPBE as the exchange functional. However, poor performance of the original vdW-DF in predicting the binding energies and intermolecular distances, are due to overestimation of the long range dispersion interaction and more repulsive character of revPBE functional [40,45]. To overcome this difficulty, a new functional called vdW-DF2 was developed using rPW86 as the exchange term and vdW2 as the nonlocal correlation term, but it was found to under estimate the C_6 coefficients [42,43]. Optimizing the exchange functionals led to better performing functionals within the vdW-DF family [40,41]. These functionals include optimized PBE (optPBE), optimized Becke88 (optB88) and optimized Becke86b (optB86b) etc. For all the above functionals the difference lies only in their exchange term, except for vdW-DF2 where there is a change in the correlation part also.

Recent theoretical studies, of adsorption of benzene on transition metal surfaces which includes both reactive and coinage metals by Yildrim et al. [46] and Carassco et al. [47], give adsorption energies that are in good agreement with the available experimental data. Yildrim et al. explore the performance of various vdW functionals in describing the adsorption process. The vdW-DF and vdW-DF2 functionals are found to give poor adsorption energies, while the optimized functionals like optPBE-vdW and optB88-vdW, were found to be good in agreement with the measured adsorption energies. Carassco et al. have computed the contribution of attractive nonlocal correlation part to the total adsorption energy for all vdW-DF functionals and found that its magnitude exceeds the total adsorption energy. Based on this they define how repulsive a given functional is and conclude that vdW-DF2 is the most repulsive and optB86b-vdW is least repulsive and the other three functionals vdW-DF, optPBE-vdW and optB88-vdW are intermediate.

All the studies mentioned above in context of vdW-DF method were carried out on the (1 1 1) surface of transition metals with fcc structure, on the bridge30 site, which is reported in many instances as the most stable adsorption site. Experimental results using different techniques are yet unsure about the most favored adsorption site on a surface, as in the case of Rh (1 1 1). In this case, HREELS shows equal preference for bridge and hollow site [14], while LEED studies project the bridge site as the most favored. In such situations, one cannot be guided by intuition that the favored site is bridge30, especially on non-fcc derived facets. Here, DFT calculations can prove to be a valuable tool to provide clarity on the favored adsorption site.

In the present study, adsorption of benzene on (1 1 1) surface of fcc metals like Pt, Pd, Rh, Ir, Ni and Ag, (1 1 0) surface of bcc metals like Mo, W and (0 0 0 1) surface of Ru are studied using plane wave DFT, with vdW interaction. Metals like Ru, Mo, and W are also important as catalyst surfaces during hydrogenation. The hcp metal Ru (0 0 0 1) surface has a structure similar to (1 1 1) facet of fcc crystal. The bare (1 1 0) surface of Mo and W are highly reactive, so their catalytic properties are modified by adding silicon, nickel etc to act as good catalyst for hydrogenation [11]. The (1 1 0) surface of the bcc structure has the highest atomic density and is quasi-hexagonal. We have also done adsorption studies on the ferromagnetic metal like Ni and on coinage metal Ag. This covers a broad range of transition metal surfaces, having facets with hexagonal symmetry. In this paper, we describe the systems studied and computational details in the following section, after which we present our results and discuss the same in light of existing literature. Finally we summarize and conclude in the last section.

2. Computational method

All calculations reported in this paper are carried out using VASP code [48,49]. The electron–ion interaction is included by using ultrasoft pseudopotential along with Projector Augmented Wave (PAW) method [50]. To account for electron-electron exchange and correlation interaction, the PBE functional [51] is employed. The dispersive forces are included using the optimized vdW-DF functionals of vdW-DF family. The metal surface was modeled as a slab of fixed number of layers, the minimum number of which is fixed by checking convergence of surface energy to within 1 meV. For the sampling of Brillouin zone a Monkhorst-Pack grid [52] of 15 × 15 × 15 for bulk calculations and 5 × 5 × 1 for slab calculations were used. The slab calculations used a Methfessel-Paxton [53] type of smearing with a width of 0.05 eV. The energy cutoff for plane waves is fixed to 400 eV. The bulk lattice parameter used for constructing the metal surface is obtained by minimizing the total energy with respect to the lattice parameter. Adsorption energy calculations are done on a 5 layer (3 × 3) unit cell slab, each layer containing nine atoms corresponding to a 0.11 monolayer (ML) surface coverage of benzene. A vacuum thickness of 15 Å is used to neglect the interaction of the molecule with periodic images of the slab. As shown in Fig. 1(a), there are four high symmetry sites available on a fcc (1 1 1) surface for benzene adsorption. These are labeled as bridge (centre of benzene in between 2 surface atoms), hcp hollow (between 3 atom with benzene centre overlapping an atom of the second layer, fcc hollow (between 3 atom with benzene centre overlapping a third layer atom) and atop. On each site, Benzene has two orientations of 0°