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Mixed aromatic-alkyne system on Pd surface – a first-principles study

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Abstract

Chemistry of mixed aromatic-alkyne systems on a metal surface is of general interest in many industrial processes. We use Density Functional Theory (DFT) to investigate the chemistry of one such system, i.e., 1,4-diphenyl-butadiyne, or DPB, in contact with Pd (110) and (111) surfaces. Reaction pathways and energetics of important processes are explored, including H₂ adsorption, dissociation and migration on the metal surface, DPB-metal interaction, the energetics of H uptake, and the effects of impurities like CO and CO₂ on H chemistry. We find that: (i) strong aromatic-metal interaction leads to significant binding strength of DPB molecule to both Pd surfaces, especially the (110); (ii) H₂ molecule readily dissociates on the Pd surface into H-radicals, which get taken up by alkyne triple bonds; (iii) CO has strong binding to the metal surface, but interacts weakly with H radicals; (iv) CO₂ binds weakly to the metal surface, but could potentially lead to interesting chemical reactions with H.

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1. Introduction

Mixed aromatic-alkyne molecules on metal surfaces are chemically interesting and could have many potential industrial applications. One obvious application is removing chemical radicals from catalyst surfaces and storing them into the unsaturated bonds of the alkyne part, while the aromatic part keeps the whole molecule bound to the catalyst surface. An important specific example of such systems are molecules that are designed to scavenge and store hydrogen^{1,2} in order to prevent explosive situations due to hydrogen build up in sealed items such as electronics, heat-exchange equipment, vacuum maintenance, battery-operated devices and so on. Two of the most successful molecules designed for this purpose are 1,4-bis (phenylethynyl) benzene (DEB)^{1,2} and its close variant 1,4-diphenyl-butadiyne (DPB). Both are dialkyne, i.e., each molecule contains two triple bonds (see Fig. 1(a) for DPB), and therefore can uptake four molecules of H₂. Previous experiments with DEB indicated that its H-uptake action is unaffected by toluene, hexane, acetone and methanol. However, impurities like CO and a few chlorinated compounds (like carbon tetrachloride, trichloroethylene, trichloroethane, chloroform, and methylene chloride) did appear to inhibit or reduce the hydrogen uptake capability.² A better understanding of the action of impurities is clearly necessary in order to prevent the loss of H-uptake effectiveness.

While DFT calculations of molecular adsorption on crystal surfaces have now become standard,^{3,4} to our knowledge not much work exists on the action of DEB or DPB, or the chemistry of mixed aromatic-aliphatic system on a metal surface in general. This paper discusses our initial DFT calculations of DPB molecules on Pd (110) and (111) surfaces. More specifically we look into adsorption, dissociation and migration of hydrogen on the metal surface, interaction of DPB with metal, the energetics of H uptake by DPB from the metal, as well as the effect of impurities like CO and CO₂ on the H-uptake action of DPB.

2. DFT Methodology

For the DFT code we used DMol³ from Accelrys,⁵⁻⁷ which employs localized basis sets defined on a numerical grid, and can be used both with molecules⁶ and with periodic supercells,⁷ the latter being necessary in this work for representing periodic metal surfaces. Within DMol³ the electronic wave functions were expanded in a double-numeric polarized (DNP) basis set truncated at a real-space cutoff of 4.0 Å and represented on a “medium”

numerical grid. The core electrons of the Pd atoms were represented by the recently developed Density-Functional Semi-core Pseudopotentials (DSPP),⁸ while all other electrons were represented explicitly. A nonlocal DFT Hamiltonian was used with gradient-corrected exchange-correlation functional due to Perdew, Burke, and Ernzerhof (PBE).⁹ For calculations employing periodic supercells accurate Brillouin zone sampling was ensured by summing over a finite set of K-points chosen according to the Monkhorst-Pack scheme¹⁰ with a grid spacing of $0.05 \text{ \AA}^{-1}$. For certain reactions, accurate transition state barriers were obtained by a generalized synchronous transit method recently extended to periodic supercells.¹¹

3. Molecular models

Fig. 1(a) displays the atomic model of a DPB molecule. It consists of two phenyl rings sandwiching an unsaturated aliphatic chain of four C atoms with two triple bonds. The H-uptake action could happen either by direct dissociation of H_2 across an unsaturated bond in the alkyne part of DPB or initial dissociation and chemisorption of H_2 on the Pd surface, followed by the uptake of H by a DPB molecules adjacent to the metal surface. In this study we confine ourselves to the second mechanism, which strongly brings out the catalytic action of the Pd surface. Also for concreteness we perform all our calculations on two of the most commonly studied surfaces of Pd, i.e., the (110) and (111) surfaces. Both surfaces were cleaved from the experimental fcc crystal structure of lattice constant $3.89 \text{ \AA}$, and were modeled with three atomic layers with the bottom two layers constrained at the bulk position in order to mimic the presence of a larger number of layers in real metal particles (Fig. 1(b-e)). For most simulations on the (110) surface, a 2×3 extended surface with orthogonal dimensions of $7.78 \text{ \AA} \times 8.25 \text{ \AA}$ in the surface plane was employed (Fig. 1(b, c)), while for the (111) a 3×3 extended surface with dimensions $8.25 \text{ \AA} \times 8.25 \text{ \AA}$ and an in-plane cell-angle of 120° was used (Fig. 1(d, e)). DPB, however, is an extended molecule, and computing its binding geometry and energy necessitated a more extended 5×4 supercell in the surface plane for both surfaces (see Fig. 3). All supercells included a vacuum of $20 \text{ \AA}$ normal to the plane in order to minimize interaction from translationally periodic images. For investigating binding energies to the DPB in the gas phase we employed DMol³ without periodic boundary conditions.

4. Results

Table 1 lists the computed binding energies of various molecules on the metal surface, while Table 2 displays the reaction heats (at $T = 0$) for some of the relevant processes. The main results for (110) are summarized below, with (111) results compared at the end.

1. Pd (110) surface consists of rows of atoms (along the OB direction in Figs. 1(b) and (c)) with an interatomic separation of 2.75 Å along the rows. The inter-row separation is 3.89 Å. Most energetically stable adsorbate structures occur on the top of a Pd atom or symmetrically above two successive Pd atoms along these rows. Below, these adsorbate configurations are referred to *top-atom* and *mid-row* respectively (see H₂ molecule in Fig. 2(a) as an example of *top-atom* configuration, and H-atoms in Fig. 2(b) as examples of *mid-row* configuration). For almost all adsorbate structures we find only a small relaxation of the top Pd layer from its unrelaxed as-cleaved geometry.
2. A H₂ molecule physisorbs in the top-atom configuration (Fig. 2(a)) and has substantial binding ~ 9.4 kcal/mol. It is energetically favorable (by 7.1 kcal/mol) for the H-H bond to break and for the H₂ molecule to dissociate into two H radicals, each bonding in successive mid-row sites along the same row (Fig. 2(b)). The dissociation process has a small barrier, 6.4 kcal/mol, which could be easily overcome at room temperature. Each H radical can diffuse easily along the rows, with a migration barrier of only 6.5 kcal/mol. Migration should also be possible perpendicular to the Pd-rows, likely involving the second-layer subsurface atoms. The important point from these results is that H₂ should dissociate and migrate readily on the Pd surface, although more accurate values of the dissociation and migration barriers require including quantum effects of the H nuclei. Such effects have been studied in detail for Pd (100)¹² and Pd (111)¹³ surfaces.
3. H₂ uptake by DPB happens in the unsaturated bonds of the aliphatic C in the middle. A H₂ molecule gains $43.1 - 16.5 = 26.6$ kcal/mol by moving from the metal surface into an unsaturated bond in the middle of the alkyne part of DPB (see Tables 1 and 2), explaining its hydrogen scavenging action.
4. Instead of attacking an unsaturated bond (see point 3 above) a H₂ molecule (or 2 H radicals from the Pd surface) could bind across the phenyl-aliphatic bond of DPB, with the latter dissociating into a benzene and a 1-phenyl-

butadiyne fragment. Even though this process involves the cleaving of a C-C bond, it is actually an exothermic process in the gas phase (see Table 2).

5. Most of the binding of DPB to the Pd surface arises out of the strong binding of the end phenyl groups to the metal surface. In fact upon structural relaxation of the DPB molecule on the Pd surface the two central atoms in the dialkyne part of the molecule appears to lift from the metal surface (see Fig. 3), resulting in a net binding smaller than two times the binding of individual benzene rings to the surface. This feature appears true for both (110) and (111) surfaces.
6. CO binds very strongly to the metal surface in the mid-row configuration, with the C bonding directly to neighboring Pd atoms along a row and the O sticking out normal to the Pd surface as in a carbonyl group (Fig. 4(a, b)).^{14,15} This CO group reacts weakly with freely migrating H radicals on the metal surface. For instance, it does not form a stable aldehyde, and formation of an alcohol is a highly endothermic process (see Table 2). The net binding of a CO group and a H radical in successive mid-row positions along the same row is approximately equal to the sum of binding energies of the individual adsorbates in the absence of the other, which further points to weak interaction between the CO and H.
7. Due to strong binding to the metal, the CO is unlikely to leave the metal surface altogether in favor of DPB. However, it is possible for the O to form a bridge between an unsaturated C of DPB and the original C it was double-bonded to. Such a process would potentially reduce the efficiency of DPB in taking up H. Further simulations are necessary to investigate the energetic feasibility of this process.
8. Finally, we find that CO₂ interacts weakly with the Pd surface, in agreement with previous B3LYP calculations on Pd(111).¹⁶ However, once adsorbed, a CO₂ molecule can interact strongly with a H radical on the metal surface resulting in CO and OH groups bonded to the surface. It was not possible for us to explore all possible structures that might form. Fig. 5 shows our lowest-energy structure, which is energetically favorable by 9.0 kcal/mol as compared to the original CO₂ molecule reacting with a H radical on the Pd surface. The structure in Fig. 5 involves a CO in the same configuration as in Fig. 4 (see point 6 above), while the O-atom of the OH sits in the mid-row position of a neighboring Pd-row with the Pd-O-H angle being $\sim 104^\circ$. The OH group can

subsequently interact with a second H radical and release a water molecule to the atmosphere with a small energy cost of 4.4 kcal/mol.

As evident from Tables 1 and 2, the above discussion also holds for the (111) surface, except that some of the energy values are different. Most significant is the fact that the binding energy of a benzene ring to the (111) surface is more than 10 kcal/mol lower on the (111) surface, and the resulting binding of DPB is lower by 25 kcal/mol as compared to binding on the (110) surface. The formation of alcohol, on the other hand, is a more stable process on the (111) surface by more than 8 kcal/mol, although the process of forming alcohol is still endothermic by 23.6 kcal/mol (see Table 2). The last three rows of Table 2 also show a delicate balance of reaction energies. Thus, the reaction $\text{CO}_2/\text{Pd} + \text{H}/\text{Pd} \rightarrow \text{CO}/\text{Pd} + \text{OH}/\text{Pd}$ becomes endothermic on (111), while the reaction $\text{OH}/\text{Pd} + \text{H}/\text{Pd} \rightarrow \text{Pd} + \text{H}_2\text{O (gas)}$ becomes exothermic, exactly opposite to the corresponding reactions on (110). However, the net reaction $\text{CO}_2/\text{Pd} + 2\text{H}/\text{Pd} \rightarrow \text{CO}/\text{Pd} + \text{H}_2\text{O (gas)}$ remains slightly exothermic.

5. Summary and future work

Using the (110) and (111) surfaces of Pd as a concrete model of catalytic metal surface, we investigated the hydrogen scavenging action of DPB molecules, and explored how it could be possibly affected by the presence of poisoning agents like CO and CO_2 . The calculations reveal that H_2 should easily dissociate on the Pd surface and the resulting H radicals should diffuse freely, in agreement with more accurate calculations incorporating quantum effects of H nuclei.^{12,13} The hydrogen radicals have a strong propensity to bind across the unsaturated bonds in the aliphatic part of DPB, explaining its H scavenging action. Interestingly, it is also energetically feasible for hydrogen to cleave the phenyl-aliphatic C-C linkage, and the resulting benzene could be released to the surrounding medium at elevated temperatures. CO adsorbs strongly on the metal surface as well, but interacts weakly with H_2 or the freely diffusing H radicals. However, the adsorbed CO could potentially reduce the effectiveness of DPB in several ways, like: (i) blocking possible binding sites of DPB on the metal surface; and (ii) directly forming a O-bridge with an unsaturated C-atom of DPB. CO_2 binds weakly to the Pd surface, but can potentially lead to the release of H atoms in the form water molecules to the surrounding environment. Further work is necessary to investigate the

feasibility of O-bridge formation between DPB and the metal-bound C-atom, and also how the structural modification of DPB due to the first H₂ adsorption affects its stability on the metal surface and the uptake of subsequent hydrogen. Finally, small nanoclusters of Pd could provide interesting reaction sites not present on the (110) or (111) surfaces, and would require further thought and simulations.

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Table 1: Binding energy of various species on Pd (110) and (111) surfaces. Computed energy barriers for H₂ dissociation and surface diffusion of H radicals on Pd (110) are also indicated.

System	$E_{binding}$ to Pd (110) (kcal/mol)	$E_{binding}$ to Pd (111) (kcal/mol)
H ₂ (physisorbed)	9.4	4.2
H ₂ (dissociated)*	16.5	19.3
DPB**	66.0	41.0
Benzene	36.5	24.4
CO	44.7	41.7
COH (alcohol)***	19.5	27.8
CO ₂	4.4	2.2

*On (110) surface $\Delta E_{dissociation}^{barrier} \sim 6.4$ kcal/mol, $\Delta E_{diffusion}^{barrier} \sim 6.5$ kcal/mol

**Calculations performed on a (5x4) extended surface of both (110) and (111)

***Binding with respect to an isolated CO molecule and isolated ½ H₂ molecule

Table 2: Computed heats of reaction (at $T = 0$) for relevant processes on Pd(110) and Pd(111). Species on metal surface are explicitly indicated with a “/Pd” extension. Negative (positive) $\Delta E_{reaction}$ indicates exothermic (endothermic) process.

Reaction	$\Delta E_{reaction}$ (kcal/mol)	
	(110)	(111)
H ₂ insertion into a DPB (alkyne $\rightarrow$ alkene)	- 43.1	
H ₂ (gas) + DPB $\rightarrow$ benzene + 1-phenyl-butadiyne	- 2.5	
CO/Pd + H/Pd $\rightarrow$ COH/Pd (alcohol)	+ 33.4	+ 23.6
CO ₂ /Pd + H/Pd $\rightarrow$ CO/Pd + OH/Pd	- 9.0	+ 3.4
OH/Pd + H/Pd $\rightarrow$ Pd + H ₂ O (gas)	+ 4.4	- 5.0
CO ₂ /Pd + 2H/Pd $\rightarrow$ CO/Pd + H ₂ O (gas)	- 4.6	- 1.6

Figure Captions:

Figure 1. (a) Molecular structure of DPB; (b) & (c) Pd (110) 2x3 surface shown in top and side views; (d) & (e) Pd (111) 3x3 surface shown in top and side views. The top layer Pd atoms are shown in ball representation for clarity. This layer is allowed to relax in our simulations while the two subsurface layers (atoms shown in cross) are constrained. For simulations of DPB binding a more extended 5x4 surface is used for both (110) and (111) (see Fig. 2).

Figure 2. (a) H₂ physisorption; and (b) H₂ dissociation on Pd (110) shown in top-view. The H-atoms are shown in small white balls. The physisorption occurs at a *top-atom* site, while immediately upon dissociation the H-atoms occupy successive *mid-row* positions along the same Pd-row. The dissociation is an exothermic process, but entails a small energy barrier of ~ 6.4 kcal/mol.

Figure 3. DPB molecule adsorbed on: (a) Pd (110) surface; (b) Pd (111) surface. The binding energy is weaker to the (111) surface. In both cases, the two central C-atoms of the dialkyn part get lifted from the metal surface.

Figure 4. CO adsorption on Pd(110): (a) side-top view; (b) side view. The C and O atoms are labeled in (b). The C atom is at a mid-row site symmetrically equidistant from neighboring Pd-atoms along a row, while the O-atom sticks out normal to the surface. This configuration has strong binding to both the (110) and (111) surfaces (see Table 1), and can effectively block metal sites from H₂ adsorption, dissociation, and metal interaction with DPB.

Figure 5. Possible low-energy structure resulting from the reaction of a weakly bound CO₂ with a freely diffusing H-radical on the Pd(110) surface. The CO fragment is in the configuration described in Figure 4, while the O-atom of the OH is in a mid-row site of a neighboring Pd-row. The Pd-O-H angle is $\sim 104^\circ$. The C, O and H atoms are indicated with labels.

Figure 1

(a)

(b)

Figure 2

(a)

(b)

Figure 3

(a)

(b)

Figure 4

Figure 5