Mixed Aromatic−Alkyne System on a Pd Surface: A First-Principles Study[†]

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The 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 (DPB) in contact with Pd(110) and Pd(111) surfaces). Reaction pathways and the energetics of important processes are explored, including H_2 adsorption, dissociation and migration on the metal surface, the DPB−metal interaction, the energetics of H uptake, and the effects of impurities such as CO and CO_2 on H chemistry. We find that (i) strong aromatic−metal interaction leads to significant binding strength of the DPB molecule to both Pd surfaces, especially the (110); (ii) H_2 molecules readily dissociate 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; and (iv) CO_2 binds weakly to the metal surface, but could potentially lead to interesting chemical reactions with H.

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 in 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] to prevent explosive situations caused by 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 Figure 1a for DPB), and therefore they can uptake four molecules of H_2. Previous experiments with DEB indicated that its H-uptake action is unaffected by toluene, hexane, acetone, and methanol. However, impurities such as CO and a few chlorinated compounds (like carbon tetrachloride, tricholoro-ethylene, tricholoroethane, choloroform, 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 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 systems on metal surfaces in general. This paper discusses our DFT calculations of DPB molecules on Pd(110) and Pd(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, and the effect of impurities such as CO and CO_2 on the H-uptake action of DPB.

2. DFT Methodology

For the DFT code we used DMol[3] from Accelrys,[5−7] which employs localized basis sets defined on a numerical grid, and can be used both with molecules[6] and with periodic supercells,[7] the latter being necessary in this work for representing periodic metal surfaces. Within DMol[3], 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 scheme[10] with a grid spacing of 0.05 $Å^{-1}$. For certain reactions, accurate transition state barriers were obtained by a generalized synchronous transit method recently extended to periodic supercells.[11]

3. Molecular Models

Figure 1a 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 by initial dissociation and chemisorption of H_2 on the Pd surface, followed by the uptake of H by 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 performed all our calculations on two of the most commonly studied surfaces of Pd: the (110) and (111) surfaces. Both surfaces were cleaved from the experimental fcc crystal structure of lattice constant 3.89 Å and were modeled with three atomic layers with the bottom two layers constrained at the bulk position to mimic the presence of the larger number of layers in real metal particles
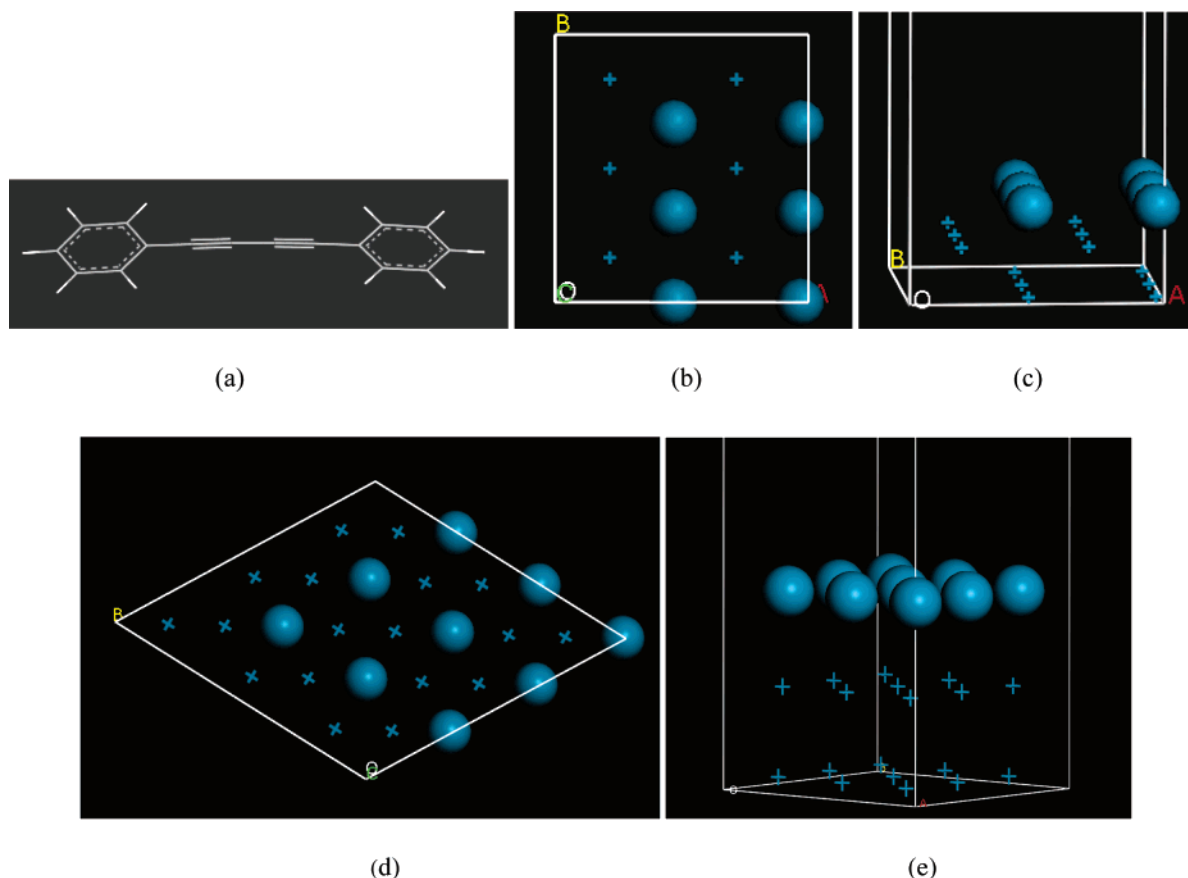
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Figure 1. (a) Molecular structure of DPB, (b, c) Pd(110) 2 × 3 surface shown in top and side views, and (d, e) Pd(111) 3 × 3 surface shown in top and side views. The top-layer Pd atoms are shown as a ball for clarity. This layer is allowed to relax in our simulations while the two subsurface layers (atoms shown as cross) are constrained. For simulations of DPB binding, a more extended 5 × 4 surface is used for both Pd(110) and Pd(111) (see Figure 2).

(Figure 1b–e). For most simulations on the (110) surface, a 2 × 3 extended surface with orthogonal dimensions of 7.78 × 8.25 Å in the surface plane was employed (Figure 1b and c), while for the (111) a 3 × 3 extended surface with dimensions of 8.25 × 8.25 Å and an in-plane cell-angle of 120° was used (Figure 1d and e). DPB, however, is an extended molecule, and computing its binding geometry and energy required a more extended 5 × 4 supercell in the surface plane for both surfaces (see Figure 3). All supercells included a vacuum of 20 Å normal to the plane to minimize interaction from translationally periodic images. For investigating binding energies to the DPB in the gas phase, we employed DMol^3 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 Pd(110) are summarized below, with Pd(111) results compared at the end.

The Pd(110) surface consists of rows of atoms (along the OB direction in Figure 1b 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 H$_2$ molecule in Figure 2a as an example of top-atom configuration, and H-atoms in Figure 2b as examples of mid-row configuration).

TABLE 1: Binding Energy of Various Species on Pd(110) and(111) Surfaces^a

system	$E_{binding}$ to Pd(110)^b (kcal/mol)	$E_{binding}$ to Pd(111) (kcal/mol)
H$_2$ (physisorbed)	9.4	4.2
H$_2$ (dissociated)	16.5	19.3
DPB^c	66.0	41.0
benzene	36.5	24.4
CO	44.7	41.7
COH (alcohol)^d	19.5	27.8
CO$_2$	4.4	2.2

^{a} Computed energy barriers for H$_2$ dissociation and surface diffusion of H radicals on Pd(110) are also indicated.[8] ^{b} On the (110) surface $\Delta E_{dissociation}^{barrier} \approx 6.4$ kcal/mol and $\Delta E_{diffusion}^{barrier} \approx 6.5$ kcal/mol. ^{c} Calculations performed on a 5 × 4 extended surface of both (110) and (111). ^{d} Binding with respect to an isolated CO molecule and isolated 1/2 H$_2$ molecule.

For almost all adsorbate structures, we find only a small relaxation of the top Pd layer from its unrelaxed as-cleaved geometry.

A H$_2$ molecule physisorbs in the top-atom configuration (Figure 2a) and has a substantial binding of ∼9.4 kcal/mol. It is energetically favorable (by 7.1 kcal/mol) for the H−H bond to break and for the H$_2$ molecule to dissociate into two H radicals, each bonding in successive mid-row sites along the same row (Figure 2b). 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

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TABLE 2: Computed Heats of Reaction (at $T = 0$) for Relevant Processes on Pd(110) and Pd(111)^a

| | $\Delta E_{reaction}$ (kcal/mol) | |
reaction	Pd(110)	Pd(111)
H$_2$ insertion into a DPB (alkyne → alkene)	−43.1	
H$_2$ (gas) + DPB → benzene + 1-phenyl-butadiyne	−2.5	
CO/Pd + H/Pd → COH/Pd (alcohol)	+33.4	+23.6
CO$_2$/Pd + H/Pd → CO/Pd + OH/Pd	−9.0	+3.4
OH/Pd + H/Pd → Pd + H$_2$O (gas)	+4.4	−5.0
CO$_2$/Pd + 2H/Pd → CO/Pd + H$_2$O (gas)	−4.6	−1.6

^{a} Species on metal surface are explicitly indicated with a "/Pd" extension. Negative (positive) $\Delta E_{reaction}$ indicates an exothermic (endothermic) process.

these results is that H$_2$ 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.

H$_2$ uptake by DPB happens in the unsaturated bonds of the aliphatic carbon atoms "sandwiched" between the two aromatic phenyl groups. A H$_2$ 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.

Instead of attacking an unsaturated bond (see point 3 above) a H$_2$ 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).

Most of the binding of DPB to the Pd surface is the result 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 Figure 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.

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
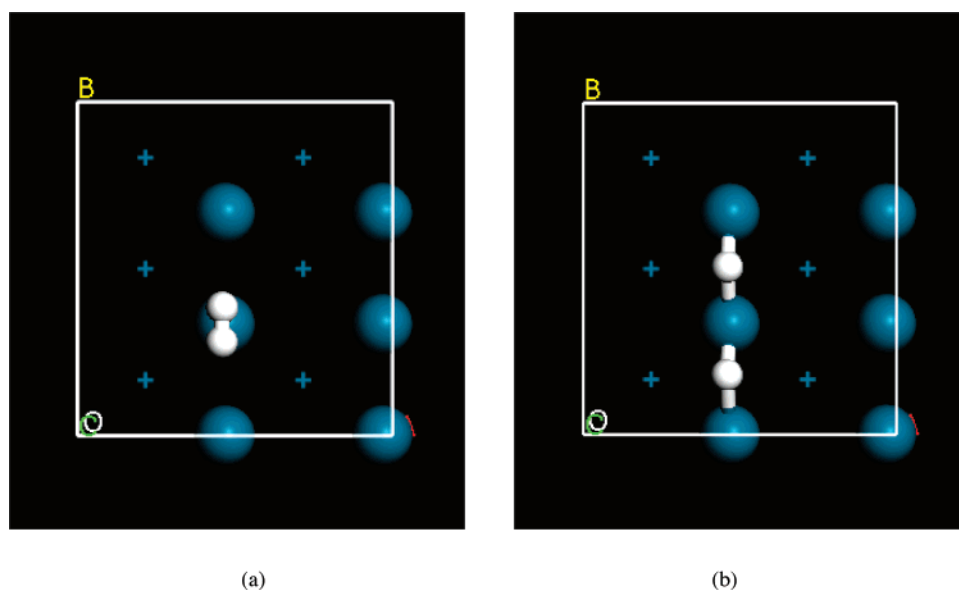

(a)　　　　　　　　　　　　　　(b)

Figure 2. (a) H$_2$ physisorption and (b) H$_2$ dissociation on Pd(110) shown as a top view. The H atoms are shown in small white balls. 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.
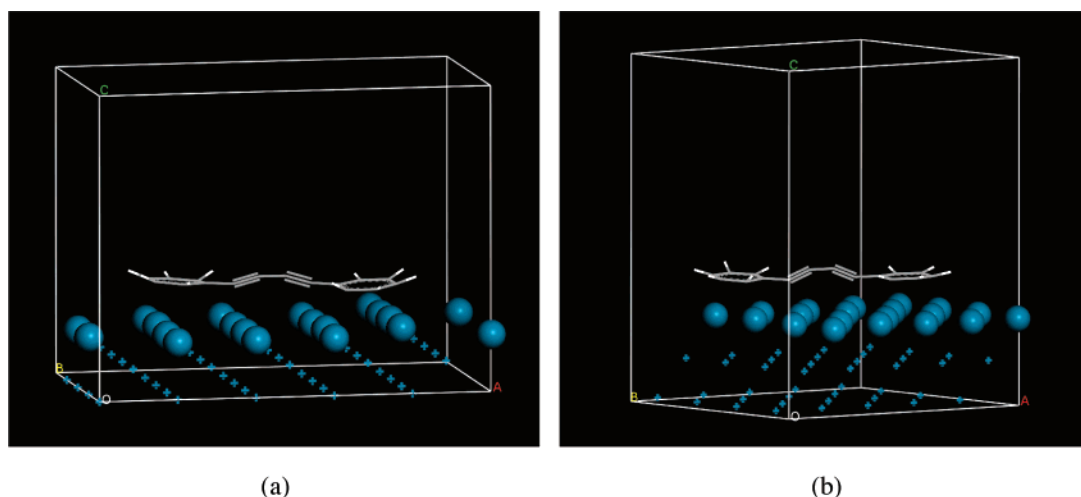

(a)　　　　　　　　　　　　　　(b)

Figure 3. DPB molecule adsorbed on (a) the Pd(110) surface and (b) Pd(111) surface. The binding energy is weaker to the Pd(111) surface. In both cases, the two central C atoms of the dialkyne part get lifted from the metal surface.
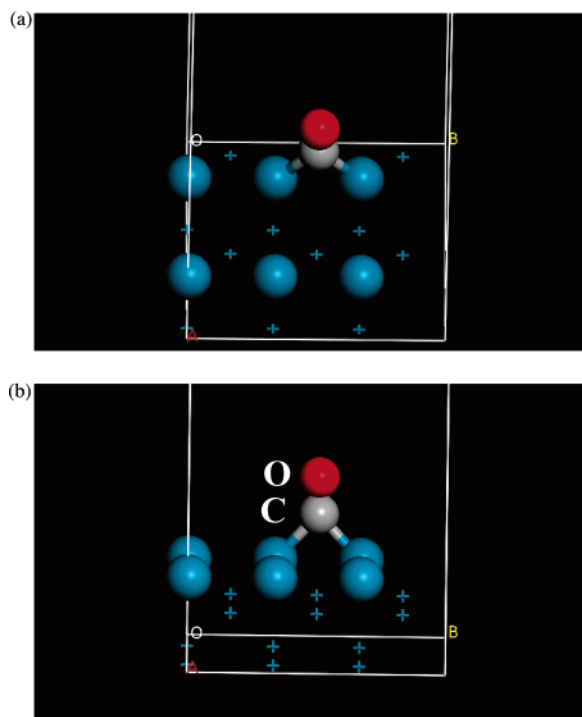
Figure 4. CO adsorption on Pd(110): (a) side−top view and (b) side view. The C and O atoms are labeled in panel b. The C atom is at a mid-row site symmetrically equidistant from neighboring Pd atoms along a row, while the O atom sticks out normal to the surface. This configuration has strong binding to both the Pd(110) and Pd(111) surfaces (see Table 1) and can effectively block metal sites from H_2 adsorption, dissociation, and metal interaction with DPB.

surface as in a carbonyl group (Figure 4a and 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 a weak interaction between the CO and H.

Because of 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 to which it was double-bonded. 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.

Finally, we find that CO_2 interacts weakly with the Pd surface, in agreement with previous B3LYP calculations on Pd(111).[16] However, once adsorbed, a CO_2 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. Figure 5 shows our lowest-energy structure, which is energetically favorable by 9.0 kcal/mol as compared to the original CO_2 molecule reacting with a H radical on the Pd surface. The structure in Figure 5 involves a CO in the same configuration as in Figure 4, 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 ∼104°. 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 is evident from Tables 1 and 2, the above discussion also holds for the Pd(111) surface, except that some of the energy
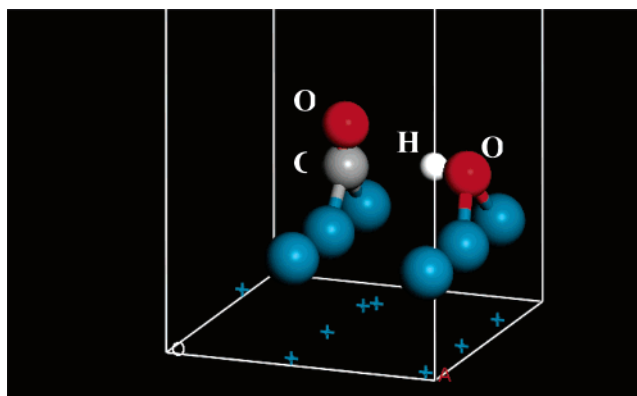

Figure 5. Possible low-energy structure resulting from the reaction of a weakly bound CO_2 with a freely diffusing H radical on the Pd(110) surface. The CO fragment is in the configuration described in Figure 4, while the O atom of the OH is in a mid-row site of a neighboring Pd row. The Pd−O−H angle is ∼104°. The C, O, and H atoms are indicated with labels.

values are different. Most significant is the fact that the binding energy of a benzene ring to the Pd(111) surface is more than 10 kcal/mol lower on the Pd(111) surface, and the resulting binding of DPB is lower by 25 kcal/mol compared to binding on the Pd(110) surface. The formation of alcohol, on the other hand, is a more stable process on the Pd(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 $CO_2/Pd + H/Pd \rightarrow CO/Pd + OH/Pd$ becomes endothermic on Pd(111), while the reaction $OH/Pd + H/Pd \rightarrow Pd + H_2O$ (gas) becomes exothermic, exactly the opposite of the corresponding reactions on Pd(110). However, the net reaction $CO_2/Pd + 2H/Pd \rightarrow CO/Pd + H_2O$ (gas) remains slightly exothermic.

5. Summary and Future Work

Using the (110) and (111) surfaces of Pd as a concrete model of a 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 such as CO and CO_2. The calculations reveal that H_2 should easily dissociate on the Pd surfaces and that the resulting H radicals should diffuse freely, in agreement with more accurate calculations incorporating the 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 it 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, for example (i) blocking possible binding sites of DPB on the metal surface and (ii) directly forming an 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 of 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 how the structural modification of DPB because of the first H_2 adsorption affects its stability on the metal surface and the uptake of subsequent hydrogen. Finally, small nanoclusters of Pd could

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provide interesting reaction sites not present on the (110) or (111) Pd surfaces and would require further thought and simulations.

References and Notes

(1) Balazs, B.; Toupadakis, A.; Beat, T.; Chambers, D.; LeMay, J. LLNL Internal Report UCRL-UR-138400; Lawrence Livermore National Laboratory: Livermore, CA, 2000.

(2) Stone, M.; Orme, C.; Peterson, E.; Kaszuba, J.; Mroz, E.; Haga, M. LANL Report LA-UR-04-0026; Los Alamos National Laboratory: Los Alamos, NM, 2004.

(3) For a recent review, see: Liu, Z. P. *Pure Appl. Chem.* **2004**, *76*, 2069 and references therein.

(4) Hill, J. R.; Subramanian, L.; Maiti, A. *Molecular Modeling Techniques in Material Sciences*; CRC Press, Taylor and Francis: Boca Raton, FL, 2005.

(5) See Accelrys webpage: http://www.accelrys.com/mstudio/ ms_modeling/dmol3.html.

(6) Delley, B. *J. Chem. Phys.* **1990***, 92*, 508.

(7) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756.

(8) Delley, B. *Phys. Rev. B* **2002**, *66*, 155125.

(9) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(10) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188.

(11) Govind, N.; Petersen, M.; Fitzgerald, G.; King-Smith, D.; Andselm, J. *Comput. Mater. Sci.* **2003**, *28*, 250.

(12) Gross, A.; Scheffler, M. *Phys. Rev. B* **1998**, *57*, 2493.

(13) Busnengo, H. F.; Crespos, C.; Dong, W.; Rayez, J. C.; Salin, A. *J. Chem. Phys.* **2002**, *116*, 9005.

(14) Mason, S. E.; Grinberg, I.; Rappe, A. M. *Phys. Rev. B* **2004**, *69*, 161401.

(15) Zhang, C. J.; Hu, P. *J. Am. Chem. Soc.* **2001**, *123*, 1166.

(16) Habas, M. P.; Mele, F.; Sodupe, M.; Illas, F. *Surf. Sci.* **1999**, *431*, 208.