Chemical reactivity on surfaces: Modeling the imide synthesis from DATP and PTCDA on Au(111)

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(Received 21 January 2010; revised manuscript received 30 January 2010; published 2 March 2010)

The role of the substrate in the formation of covalently bonded networks of adsorbed molecules is studied by density-functional theory for the recently reported case of ultrathin polyimide films formed from 4,4′-diamino-p-terphenyl (DATP) and 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) on Au(111). The surface is found to significantly modify the thermodynamics and reaction barriers of the DATP-PTCDA imidization. The experimental observation that isoimides are common for the surface-supported polymerization is traced to dispersion interactions and molecular strain that favor flat reaction intermediates.

DOI: 10.1103/PhysRevB.81.125401 PACS number(s): 68.43.−h, 71.15.Nc, 82.45.Jn

Supramolecular architectures created by self-organization and self-assembly from molecules adsorbed on metal surfaces are a field of intense research.[1] This interest is fueled by the scientific challenge to understand the driving forces for the formation of the often very complex structures as well as the hope to utilize such structures either directly or as starting point for further technological steps.[2,3]

The intermolecular interactions ranging from indirect, substrate-mediated interplay,[4] direct Coulomb forces,[2,3] weak dispersion interactions, metal complexation[5] to hydrogen,[6] or covalent bonds[7] set the stage for a large number of possibilities to form one- and two-dimensional molecular networks of varying robustness. Many potential applications of supramolecular structures, e.g., as templates in bottom-up device technology will require a thermal and chemical stability that can only be achieved by covalent bonding. Layers in which the adsorbates are interlinked by strong covalent bonds are advantageous also for applications such as organic field-effect transistors or organic solar cells. While it can be expected that the formation of covalent bonds between surface adsorbed molecules occurs differently compared to the corresponding reaction in solution or in bulk films[8]—evidenced also by calculations in the context of heterogeneous catalysis[9,10]—only little is known in detail about the impact of the surface on the reaction between the adsorbates.

Previous *first-principles* calculations have contributed much to the understanding of the interaction between single adsorbed molecules with metal substrates, see, e.g., Refs. 7 and 11–16. There are also theoretical studies that address hydrogen bonds,[17] weak direct[18] and indirect Coulomb interactions[19] as well as dispersion forces[20] between surface adsorbed molecules. In the present work we go one step further and utilize density-functional theory (DFT) to explore the impact of the surface on the chemical reaction between adsorbates. The imidization of 4,4′-diamino-p-terphenyl (DATP, cf. Figure 1) and 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) adsorbed on Au(111) (Refs. 21–23) is used as model system.

PTCDA adsorbed on coin metal surfaces is a prototypical model system for molecular adsorption studies.[14,24–27] Polyimides are a class of polymers with a wide range of applications ranging from solar-cell substrates to electronic device insulation. Recently it was demonstrated that polyimide strands can be formed from a hydrogen-bonded PTCDA-DATP superstructure on Au(111) by annealing.[22,23] From these experiments it was concluded that the confinement to the surface raises the energy barrier to form the amic acid reaction intermediate, cf. scheme in Fig. 1. In addition, isoimides were found to be common in the surface-bonded network, in contrast to solution-based and solid-state polyimide formation.

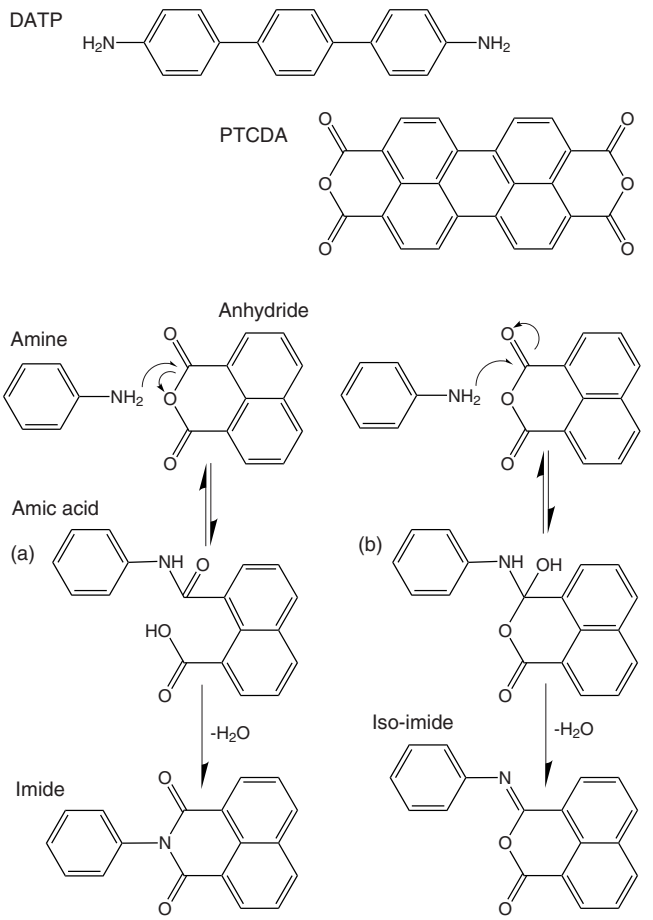

FIG. 1. Chemical structure of DATP, PTCDA, and reaction scheme of an anhydride with an amine leading to imide and isoimide products via (a) amic acid and (b) a related intermediate, respectively. From top to bottom.

The total-energy calculations presented in the following explain these findings in terms of the (mainly) van der Waals (vdW) bonding to the substrate and adsorption-induced molecular strain. It is shown that the Au(111) surface (i) modifies the reaction barriers and (ii) renders reaction intermediates, which are energetically well separated in gas phase, degenerate in energy. This favors the formation of isoimides along with imides in case of the substrate-supported reaction.

The DFT calculations are performed using the Vienna *ab initio* simulation package (VASP) (Ref. 28) and employ the PW91 functional[29] for the generalized gradient approximation to the electron exchange and correlation (XC) energy. The electron-ion interaction is described by the projector-augmented wave method,[30] which allows for a relatively moderate energy cutoff of 340 eV. The adsystem was modeled by periodically repeated supercells, containing two atomic Au layers arranged in a (6×15) translational symmetry, the adsorbed molecules and a vacuum region of 15 Å. For gold we used the calculated equilibrium lattice constant of 4.175 Å and the Brillouin-zone integrations are restricted to the Γ point. The smearing of the electronic states is performed with the Methfessel-Paxton scheme of the first order with a width of 0.2 eV.

The accurate modeling of loosely bonded adsorbates is a major challenge for DFT because the currently used XC energy functionals do not properly describe the long-range vdW interactions.[14,15,31,32] In order to account approximately for dispersion interactions, we use a semiempirical, so-called DFT-D scheme[31,32] based on the London dispersion formula. Recently benchmark calculations for a variety of small, π-conjugated molecules adsorbed on Ag(110) were performed by Blügel's group.[15] In these calculations the approximate treatment of dispersion interactions with DFT-D was compared with a more realistic vdW density-functional (vdW-DF) approach.[33] It turned out that—depending on the molecule—the calculated total adsorption energies differ by 50–200 meV. Relative energy differences calculated within either scheme agree within 30–120 meV. In our case the molecules considered are substantially larger, which will increase the error bar of the total adsorption energy. On the other hand, we compare adsorption energies of molecules with identical total formulas and rather similar adsorption geometries, which might actually reduce the error bar for energy differences. Probably 100 meV are a realistic estimate for the accuracy of energy differences calculated in our work. It should be borne in mind, however, that vdW-DF is an approximation as well, see, e.g., results in Ref. 34. Altogether, the accurate description of dispersion forces for complex systems is not satisfactorily solved.[35]

At first single adsorbed molecules are calculated. The results for PTCDA confirm earlier findings[27] that state a flat adsorption geometry and relatively weak interactions with the Au(111) surface. Indeed, the calculated potential-energy surface (PES) is only weakly corrugated, see Fig. 2. The minimum energy position, where the adsorption energy amounts to 1.21 eV (without vdW: 0.23 eV), corresponds to a geometry where the central aromatic ring adsorbs atop a H_3 surface site. The adsorption energy of DATP is similarly little site sensitive. Here, a position with the central phenyl ring in bridge position is most favorable and leads to an adsorption

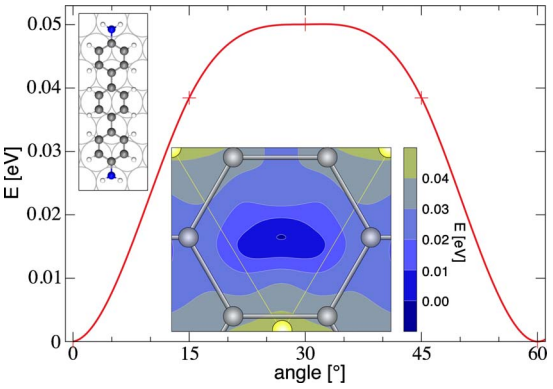

FIG. 2. (Color online) Rotational barrier calculated for DATP adsorbed on Au(111). The DATP position corresponding to 0° as well as the PES calculated for PTCDA (central aromatic ring is indicated) adsorbed on Au(111) are shown as insets. The energy scales refer to the respective most favored adsorption configurations.

energy of 1.81 eV (without vdW: 0.71 eV). Thereby, the amine group nitrogens are nearly atop gold surface atoms. In gas phase, the terminal phenyl rings and the associated amino groups are coplanar but the central phenyl ring is twisted out of this plane by 30°. The twist nearly vanishes upon adsorption on Au(111). The adsorbate reactions will be facilitated by molecular rotations. We calculate in-plane rotational barriers of about 0.05 eV for DATP, see Fig. 2. Obviously, the substrate does not noticeably hinder the lateral movements and in-plane rotations required for the polymerization.

The reaction of an aromatic amine with an aromatic anhydride proceeds by nucleophilic attack of the amine nitrogens on one of the carbonyl carbons and, following proton transfer, leads to an amic acid [intermediate (a) in Fig. 1]. Final imidization is typically achieved by thermally induced loss of water. In order to explain the common occurrence of isoimides in the molecular networks obtained from the surface-constrained imidization, Treier *et al.*[22,23] suggest an alternative reaction route—insignificant in solution—via the intermediate (b) in Fig. 1. Here, we probe the energetics of the polymerization via these two intermediates, called ACa and ACb in the following.

The calculated results are summarized in Fig. 3. The separate adsorption of PTCDA and DATP on Au(111) releases an energy of 3.02 eV. If the two molecules form the reaction intermediates ACa or ACb (cf. Fig. 4), the energy is lowered further by 0.13 eV. Within the accuracy of the calculations, both reaction intermediates are energetically degenerate at the Au(111) surface. This contrasts clearly with the energetics of the unconstrained, gas-phase intermediates, where the energy gain upon formation of ACa is substantially larger (by 0.26 eV) than for ACb, see Fig. 3. The adsorption on the surface decreases the energy difference between the two reaction intermediates by 0.13 eV even within DFT-GGA rather than DFT-D calculations. This shows that the effect discussed here is sufficiently robust not to depend on the details of the vdW approximation scheme.

Starting from ACa or ACb, a thermally induced dehydra-

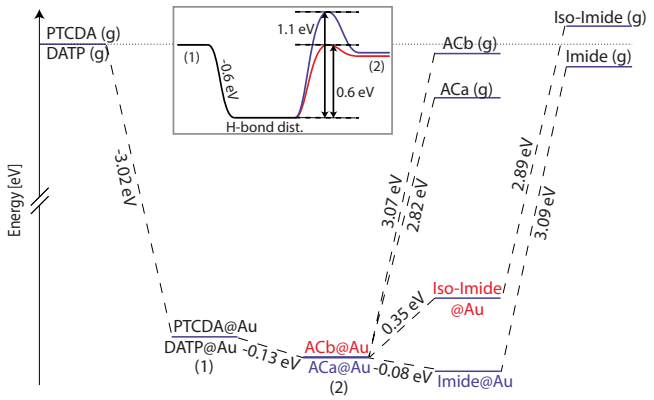

FIG. 3. (Color online) Energetics of the reaction. The inset shows the energy barriers upon the formation of the reaction intermediates ACa and ACb (2) from completely separated adsorption positions of single reactants (1). The energies for (iso-)imdides are calculated on the assumption that the water chemical potential corresponds to the energy of an isolated monomer. See text for details.

tion will lead to the formation of an imide, realizing an additional energy gain of 0.08 eV, or, at the expense of 0.35 eV, an isoimide will form. Figure 4 shows both reaction products in their most favorable adsorption geometry. The formation of an isoimide is endothermic independent of the presence of the Au(111) surface with respect to single PTCDA and DATP molecules, if the water chemical potential equals the monomer energy. It will be thermodynamically favorable, however, provided the water chemical potential is sufficiently low. This is certainly the case in the ultrahigh-vacuum experiments reported in Refs. 22 and 23. Given that the formation of an isoimide from ACa or the formation of an imide from ACb is very unlikely due to the required reorganization of strong covalent bonds, it is basically the energy barriers

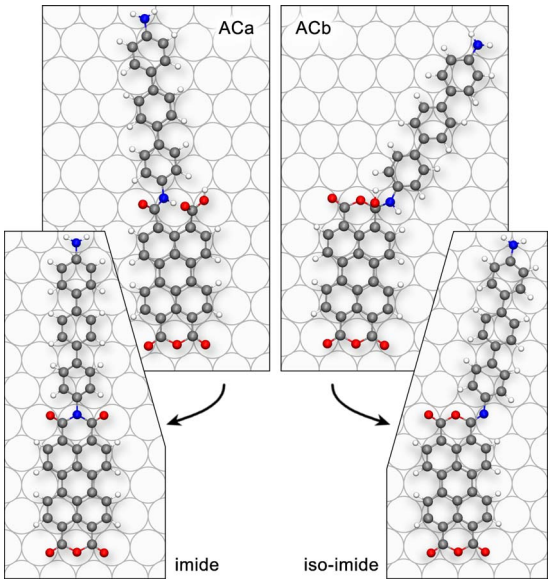

FIG. 4. (Color online) Ball and stick models of the two reaction intermediates ACa and ACb adsorbed on Au(111) in lowest-energy position. Below, the respective final reaction products, imide and isoimide, are shown.

for the formation of the respective reaction intermediates ACa and ACb that is of key importance for the formation of either imides or isoimides.

Therefore we calculate the activation energies for the formation of both reaction intermediates on the Au(111) surface. In order to cope with the large numerical expense, the PTCDA molecule was truncated to one half for these calculations, saturating the two (formerly center) carbon atoms with hydrogen. Since PTCDA adsorbs rather flat and mainly due to vdW interactions, this restriction is not likely to change the results. The five C and four H atoms of the half PTCDA farthest away from the center of the reaction were kept fixed in their optimized positions. DATP was allowed to relax freely with the exception of the first C atom, which was constrained to relaxation in a plane perpendicular to the molecular distance which served as reaction coordinate. Starting from the adsorption positions of noninteracting reactants, DATP approaches PTCDA to form either of the intermediate structures ACa or ACb. In both cases, an energy minimum is passed when DATP gets into hydrogen-bonding distance to PTCDA, see inset in Fig. 3. Upon reacting, both molecules get deformed with the DATP curling under and lifting up the PTCDA carbonyl group. The energy barrier maximum corresponds to the proton transfer from the amine group to the PTCDA oxygen. Starting from the hydrogen-bonded configuration, approximately 1.1 eV are required to activate the reaction that leads to ACa. For the formation of ACb, 0.6 eV are sufficient. Thus, while the reaction intermediates are energetically degenerate when adsorbed on the Au(111) surface, the reaction barrier required to form ACb, the starting configuration for the formation of isoimides, is lower than for ACa, the precursor of imides.

The reaction barriers calculated above are substantially influenced by the presence of the substrate. Calculations of the reaction path as described above, but without taking the surface into account, lead to energy barriers of 0.2 and 0.3 eV for the formation of ACa and ACb, respectively. Due to the many degrees of freedom of the unconstrained reaction, these values do not necessarily represent the true reaction barriers. However, they certainly prove a major impact of the Au(111) surface on the reaction kinetics.

Summarizing so far, the present calculations explain the essential features noted experimentally:[22,23] the constraint of the reaction to two dimensions (i) stabilizes the reaction intermediate ACb with respect to ACa thermodynamically, (ii) reduces the relative height of the energy barrier on the reaction path leading to ACb compared to the one leading to ACa while (iii) increasing the absolute values for both reaction barriers. The finding (iii) agrees with the measured increase in the activation temperature and the results (i) and (ii) are consistent with the experimental observation that isoimides are common when the polymerization is confined to the surface.

In order to determine the actual mechanism that causes the strong impact of the surface on the kinetics and thermodynamics of the imidization, we calculate the reactions intermediates ACa and ACb in their surface adsorbed geometries, but without taking the surface into account. It turns out that now the energetic degeneracy between the two structures is lifted and ACa is about 0.11 eV more favorable than ACb.

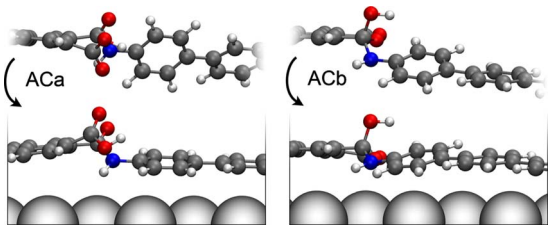

FIG. 5. (Color online) Ball and stick models of the two reaction intermediates ACa and ACb formed in gas phase (top) compared to their geometry assumed on the substrate.

Thus about 42% of the 0.26 eV energy difference between the two gas-phase tautomers ACa and ACb is consumed by the differences in the respective substrate-adsorbate bonding of the two reaction intermediates while the remaining 0.14 eV are quenched by the different amounts of surface-induced molecular strain. The different strain contributions to the energy balance are easily understood from the respective freely relaxed and surface adsorbed ACa and ACb geometries shown in Fig. 5. Upon adsorbing on the surface, the phenyl ring twist is much reduced and the carbonyl bonds are strongly reoriented for ACa, while the geometrical implications for ACb are far smaller. In fact, the average surface-induced atomic displacement within ACb amounts to only 43% of the respective value for ACa. The adsorbate-substrate interactions are nearly as important as the strain for the energetics of ACa and ACb. The dominating contribution to the molecule-surface bonding stems from vdW interactions. In fact, we find dispersion forces to be responsible for 78% and 80% of the respective total adsorption energies of ACa and ACb. The average distance between ACb and the Au surface is about 0.1 Å smaller than in case of ACa. This is due to the fact that ACb is more planar than ACa, thus allows for a more effective dispersion interaction with the gold surface.

In summary, we performed first-principles calculations in order to understand the role of the surface for the substrate-supported reaction of PTCDA and DATP on Au(111). Our results explain the characteristics found experimentally for the imidization of the surface adsorbed molecules. While the reactants can move rather freely on the surface, the vdW bonding between adsorbates and substrate favors the formation and stability of planar reaction intermediates compared to nonplanar geometries which experience a substantial strain upon surface bonding. This changes both the reaction kinetics and thermodynamics of the imidization and, thereby, renders the formation of isoimides more likely on the surface compared to solution or solid-state reactions. The present calculations elucidate in atomistic detail how spatial constraints lead to a negative and selective heterogeneous catalysis. The mechanism discussed here—possibly in combination with further effects such as electron transfer and screening—can be expected to apply to essentially all instances of substrate supported bond formation.

We thank Neville Richardson, Roman Fasel and Matthias Treier for suggesting this work and very helpful discussions. Financial support from the Deutsche Forschungsgemeinschaft as well as grants of supercomputer time by the Höchstleistungs-Rechenzentrum Stuttgart HLRS and the Paderborn Center for Parallel Computing PC^2 are gratefully acknowledged.

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