SUPPLEMENTAL INFORMATION: Steps or Terraces? Dynamics of Aromatic Hydrocarbons Adsorbed at Vicinal Metal Surfaces

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DFT CALCULATIONS

Density-functional theory calculations were performed using the all-electron full-potential FHI-aims code and numerically tabulated atom-centered orbitals (NAOs) basis set [1]. We employed self-consistent convergence criterion for the total energy, force and charge density of 10^{-4} eV, 10^{-2} eV/Å, and 10^{-5} Å^{-3}, respectively. Relativistic effects for metal atoms were treated by using the scaled zeroth-order regular approximation (ZORA). Different slabs were separated by 20 Å of vacuum to eliminate the interactions between image atoms.

The transition state for diffusion processes was searched by using the LST/QST algorithm [2], as implemented in the plane-wave basis set CASTEP code [3]. The valence electrons were expanded in plane waves with a cutoff energy of 700 eV. For slab calculations, we used a $3 \times 3 \times 1$ k-points mesh.

LOW COVERAGE CONFIGURATIONS

At low coverage, benzene (Bz) molecule was placed in the atop, hcp, fcc, and bri sites with 0° and 30° rotations. Naphthalene (Np) molecules were placed with an addition of the second aromatic ring to the 0° case, namely with the long axis molecule parallel to the Cu step edge. Note that we have systematically considered 70 initial structures for Bz/Cu(443) and 40 structures for Np/Cu(443) systems, according to their distances d between the center of the molecule and the adjacent step edges.

Figure 1 shows the stable adsorption structures for the Np/Cu(443) system, in analog to Figure 1c in the main text, which indicates molecule−substrate binding heights for Bz/Cu(443).

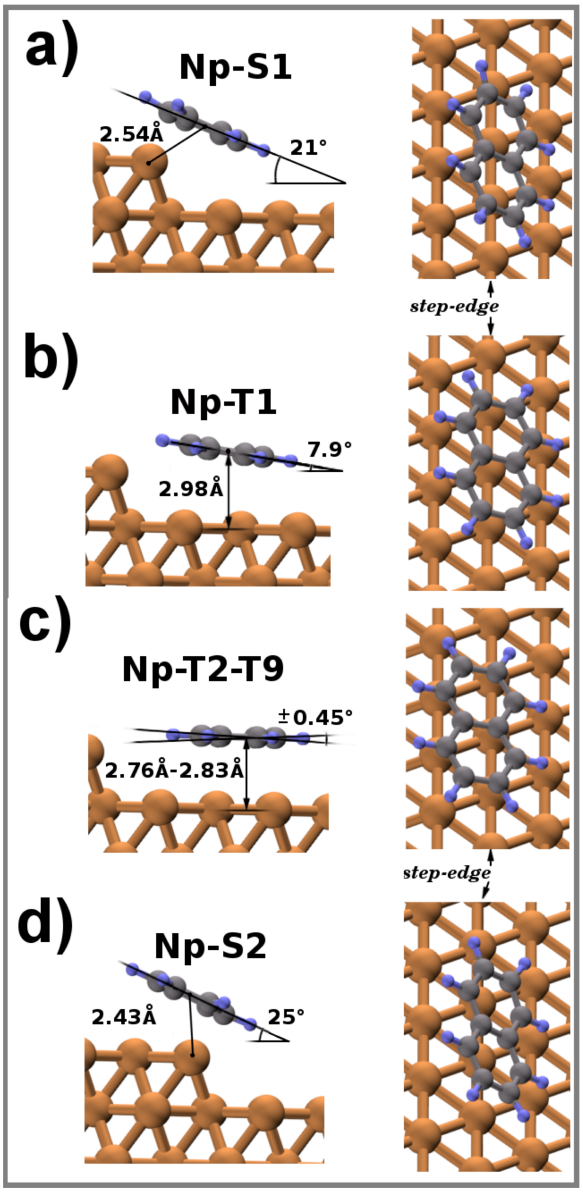

FIG. 1. Fully relaxed naphthalene structures from the PBE+vdW^{surf} method.

MONOLAYER AND MULTILAYER CONFIGURATIONS

High-coverage adsorption models considered in the present work are shown in Figure 2. All these structures were created based on the most stable Bz-S1 and Np-S1 structures (see Figures 1a and 1b in the main text). Notably, there are 3 pathways from the complete monolayer (3 molecules) to the initial bilayer (4 molecules), 6 pathways to the next bilayer coverage (5 molecules), and 3 pathways to the complete bilayer (6 molecules).

The total binding energy (*Total bE*) is defined as, $Total\ bE_n = Sys_n - surf - n \times m$, where Sys_n, $surf$, and m denote the total energies of the entire system with n molecules, the clean metal substrate, and the isolated

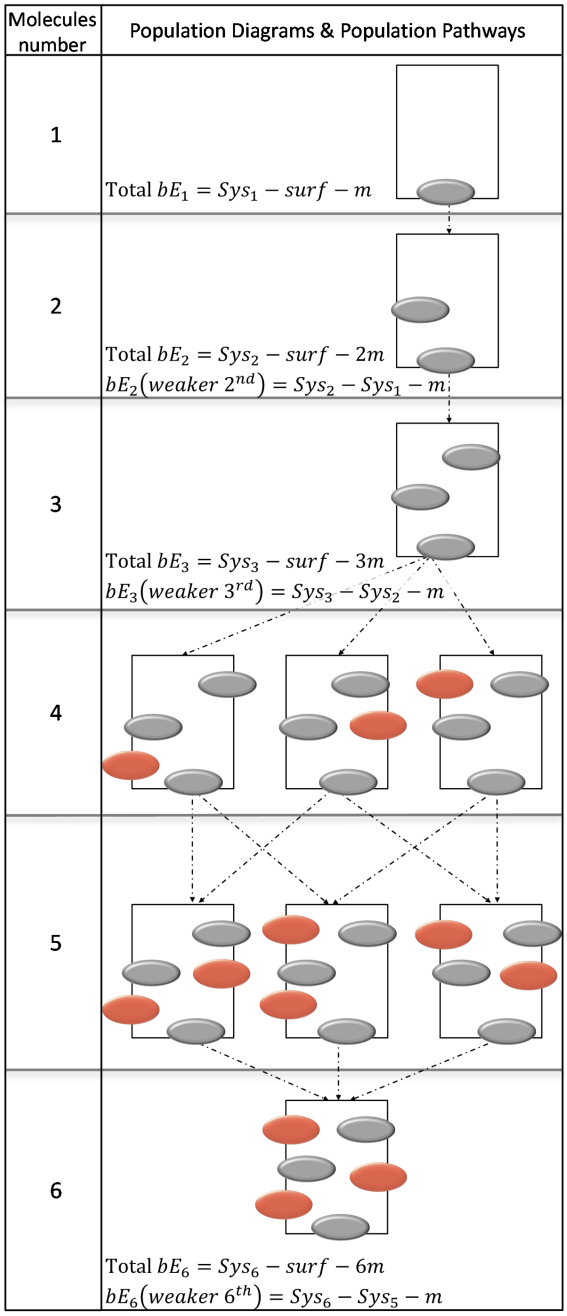

FIG. 2. Schematic plots for the population pathways evolved in the adsorption process for the mono– and bilayer coverages.

molecule, respectively. The stability of the last added molecule, n^{th}, is measured by $bE_n\ (weaker\ n^{th})$, which is defined as $bE_n\ (weaker\ n^{th}) = Sys_n - Sys_{(n-1)} - m$. The computed binding energies for Bz and Np on the Cu(443) surface at different coverages are shown in Tables I to III.

TABLE I. Binding energies calculated by PBE+vdW^{surf} for benzene and naphthalene configurations at low coverages at the Cu(443) surface.

System	Benzene B-E (eV)	Naphthalene B-E (eV)
9×1	-1.34	-2.02
8×1	-1.34	-2.00
7×1	-1.32	-2.00
6×1	-1.32	-2.05
5×1	-1.31	-2.02
4×1	-1.31	-1.99

TABLE II. Binding energies calculated by PBE+vdW^{surf} for benzene configurations at monolayer and bilayer coverages at the Cu(443) surface.

System	Molecule number	Total B-E (eV)	Weaker mol. B-E (eV)
	1	-1.32	-1.32
	2	-2.29	-0.98
	3	-3.14	-0.85
	4	-3.69	-0.55
	5	-4.55	-0.73
4×1	6	-4.47	-0.64

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[1] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, Comput. Phys. Commun. **180**, 2175 (2009).
[2] N. Govind, M. Petersen, G. Fitzgerald, D. King-Smith, and J. Andzelm, Comp. Mat. Sci. **28**, 250 (2003).
[3] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. Probert, K. Refson, and M. C. Payne, Zeitschrift für Kristallographie **220**, 567 (2005).

TABLE III. Binding energies calculated by PBE+vdW^{surf} for naphthalene configurations at monolayer and bilayer coverages at the Cu(443) surface.

System	Molecule number	Total B-E (eV)	Weaker mol. B-E (eV)
	1	-2.06	-2.06
	2	-3.50	-1.44
	3	-4.83	-1.34
	4	-5.67	-0.84
	5	-6.74	-0.90
6×1	6	-7.71	-0.97