Electronic Supplementary Material (ESI) for Nanoscale.

Adsorption of Ethylenediamine on Cu Surfaces: Attributes of a Successful Capping Molecule Using First-Principles Calculations

Electronic Supplementary Information

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Supplementary Tables

Table S1. Coverages of EDA studied on Cu(100) and Cu(111) with corresponding unit cells.

	Cu(100)			
θ (ML)	0.25	0.17	0.13	0.08
Unit Cell	(2×2)	(3×2)	(4×2)	(4×3)
	Cu(111)			
θ (ML)	0.25	0.17	0.13	0.08
Unit Cell	(2×2)	(3×2)	(4×2)	(4×3)

Table S2. Results of convergence tests on total binding energy per EDA molecule (in eV) for various *k*-point sampling, energy cutoff, and vacuum spacing at 0.25 ML coverage. Values in the shaded cells were used for the final results.

	k-point				
$\mathrm{Cu}(100) - (2 \times 2)$ *	$(9 \times 9 \times 1)$	$(10 \times 10 \times 1)$	$(11 \times 11 \times 1)$	$(12 \times 12 \times 1)$	$(13 \times 13 \times 1)$
$E_{\mathrm{bind,EDA}}$ (eV)	1.00	1.00	1.00	1.01	1.01
$\mathrm{Cu}(111) - (2 \times 2)$ *	$(10 \times 6 \times 1)$	$(11 \times 6 \times 1)$	$(10 \times 7 \times 1)$	$(11 \times 7 \times 1)$	$(12 \times 8 \times 1)$
$E_{\mathrm{bind,EDA}}$ (eV)	0.82	0.82	0.82	0.82	0.82
Energy cutoff (eV) *	450.00	475.00	500.00	525.00	550.00
$E_{\mathrm{bind,EDA}}$ (eV)	1.00	1.00	1.00	1.00	1.00
Vacuum spacing $(\mathrm{\AA})$	38.00	39.00	40.00	41.00	42.00
$E_{\mathrm{bind,EDA}}$ (eV)*	1.00	1.00	1.00	1.00	1.00

* Choices of *k*-point sampling for other coverages are made based on the results of 0.25 ML. Tests on energy cutoff and vacuum spacing are based on the $\mathrm{Cu}(100) - (2 \times 2)$ unit cell

Table S3. Key energies (in eV) of EDA adsorption configurations with the highest total binding energy on Cu(100) and Cu(111) at different coverages.

	θ (ML)	$E_{\mathrm{bind}}^{\mathrm{short}}$	$E_{\mathrm{bind}}^{\mathrm{vdW}}$	$E_{\mathrm{Ads-Cu}}^{\mathrm{short}}$	$E_{\mathrm{Ads-Cu}}^{\mathrm{vdW}}$	$E_{\mathrm{Ads-Ads}}^{\mathrm{short}}$	$E_{\mathrm{Ads-Ads}}^{\mathrm{vdW}}$
Cu(100)	0.25	0.27	0.74	0.42	0.50	-0.11	0.24
	0.17	0.45	0.56	0.52	0.51	-0.03	0.06
	0.13	0.45	0.58	0.57	0.48	-0.08	0.10
	0.08	0.53	0.52	0.62	0.52	-0.04	0.01
Cu(111)	0.25	0.16	0.66	0.24	0.41	-0.04	0.26
	0.17	0.29	0.63	0.41	0.52	-0.06	0.12
	0.13	0.29	0.59	0.41	0.50	-0.08	0.10
	0.08	0.39	0.50	0.51	0.51	-0.08	0.01

Table S4. Charges of the top layer of the Cu slab and the bound NH_2 group at different coverages of EDA. Positive numbers represent a positive charge and charge is determined based on a unit cell containing one EDA.

	Cu(100)				Cu(111)			
θ_{EDA} (ML)	0.25	0.17	0.13	0.08	0.25	0.17	0.13	0.08
Cu	0.33	0.35	0.34	0.32	0.32	0.34	0.22	0.30
NH_2	-0.28	-0.36	-0.28	-0.37	-0.32	-0.32	-0.30	-0.28

Table S5. Summary of the results for CI-NEB calculations (energy in eV). E_a is the energy difference between the energies of the initial state (E_{initial}) and the transition state (E_{TS}) and ΔE is the energy difference between the initial and final (E_{final}) states.

	E_{initial}	E_{final}	E_{TS}	ΔE	E_{a}
Cu(100)	-173.457	-173.587	-173.237	-0.130	0.22
Cu(111)	-174.611	-174.452	-173.650	0.159	0.96

Table S6. Energy decomposition (in eV) of images along the minimum-energy pathways on Cu(100) and Cu(111) in **Figure 8**.

	Image	$E_{\mathrm{EDA-Cu}}$	$E_{\mathrm{EDA-Cu}}^{\mathrm{short}}$	$E_{\mathrm{EDA-Cu}}^{\mathrm{vdW}}$	$E_{\mathrm{H_2O-Cu}}$	$E_{\mathrm{H_2O-Cu}}^{\mathrm{short}}$	$E_{\mathrm{H_2O-Cu}}^{\mathrm{vdW}}$	$E_{\mathrm{H_2O-EDA}}$	$E_{\mathrm{H_2O-EDA}}^{\mathrm{short}}$	$E_{\mathrm{H_2O-EDA}}^{\mathrm{vdW}}$
Cu(100)	0	0.87	0.38	0.49	0.03	0.02	0.01	0.69	0.51	0.18
	1	0.87	0.46	0.41	0.02	0.01	0.01	0.66	0.50	0.16
	2	0.75	0.35	0.39	0.02	0.01	0.01	0.78	0.61	0.16
	3	0.72	0.34	0.37	0.02	0.01	0.01	0.77	0.61	0.16
	4*	0.71	0.34	0.37	0.03	0.02	0.02	0.77	0.55	0.21
	5	0.73	0.36	0.37	0.04	0.02	0.02	0.81	0.59	0.22
	6	0.73	0.36	0.37	0.10	0.05	0.05	0.83	0.59	0.24
	7	0.72	0.32	0.39	0.15	0.07	0.08	0.80	0.55	0.25
Cu(111)	0	0.64	0.25	0.39	0.01	0.01	0.01	0.73	0.58	0.14
	1	0.64	0.25	0.39	0.02	0.01	0.01	0.80	0.62	0.18
	2	0.59	0.22	0.38	0.02	0.01	0.01	0.80	0.53	0.27
	3	0.59	0.14	0.45	0.04	0.02	0.02	0.62	0.30	0.32
	4*	0.54	0.09	0.45	0.14	0.06	0.08	-0.24	-0.59	0.34
	5	0.29	0.03	0.26	0.16	0.05	0.11	0.66	0.34	0.32
	6	0.22	0.04	0.18	0.24	0.06	0.18	0.79	0.57	0.22
	7	0.15	0.04	0.11	0.23	0.06	0.17	0.88	0.71	0.17

* Transition state.

$E_{\mathrm{EDA-Cu}}$, $E_{\mathrm{H_2O-Cu}}$, and $E_{\mathrm{H_2O-EDA}}$ represent the interaction of EDA with Cu, water with Cu, and water with EDA, respectively. These quantities are calculated as shown in Equations (S1) to (S3) below. $E_{\mathrm{H_2O,o}}$, $E_{\mathrm{Cu+EDA,o}}$, $E_{\mathrm{Cu+H_2O,o}}$ and $E_{\mathrm{H_2O+EDA,o}}$ are the energies of a fixed water molecule, a Cu slab with EDA, a Cu slab with the just the water molecule, and EDA with the water molecule with the same configurations as the images on the pathways.

$$E_{\mathrm{EDA-Cu}} = E_{\mathrm{EDA,o}} + E_{\mathrm{Cu,o}} - E_{\mathrm{Cu+EDA,o}} \quad \text{(S1)}$$

$$E_{\mathrm{H_2O-Cu}} = E_{\mathrm{H_2O,o}} + E_{\mathrm{Cu,o}} - E_{\mathrm{Cu+H_2O,o}} \quad \text{(S2)}$$

$$E_{\mathrm{H_2O-EDA}} = E_{\mathrm{EDA,o}} + E_{\mathrm{H_2O,o}} - E_{\mathrm{H_2O+EDA,o}} \quad \text{(S3)}$$