Supporting Information

Dehydrogenation of a Single Acetylene Molecule on the Cu(111) Surface

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Contents

Computation details

Spin-polarized periodic density functional theory (DFT) calculations were performed using the Perdew-Burke-Ernzerhof (PBE) functional[1] as implemented in the Vienna Ab-initio Simulation Package (VASP) code.[2,3] Grimme's D3 method[4] was used to account for dispersion interactions between the adsorbate and the metal substrate. The core electrons were replaced by projector augmented wave (PAW) pseudopotentials,[5] which were expanded in a plane-wave basis set with a cutoff energy of 400 eV. We utilized (4 × 4) supercells, and a Γ-centered 8 × 8 × 1 k-point grid for Brillouin zone sampling. The slab models consist of five metal layers, with all layers relaxed during ionic relaxations. The periodically replicated slabs were separated by over 15 Å of vacuum, and the dipole correction was applied to avoid interactions between periodic slab images. The convergence criteria for the electronic self-consistent iterations and ionic relaxations were 10^{-7} eV and 0.01 eV/Å, respectively.

The adsorption energy was calculated using the following equation:

$$E_{\mathrm{ad}} = E_{\mathrm{surface + adsorbate}} - (E_{\mathrm{surface}} + E_{\mathrm{adsorbate}})$$

The calculated values are summarized in Table S1.

Table S1. Comparison of the calculated adsorption energy E_{ad} (eV) for all molecules studied in this work.

	C_2H_2	C_2H	C_2	H atom
Cu(111)	−1.64	−4.32	−6.24	−2.62
Cu(100)	−1.78	−4.71	−6.55	−2.53

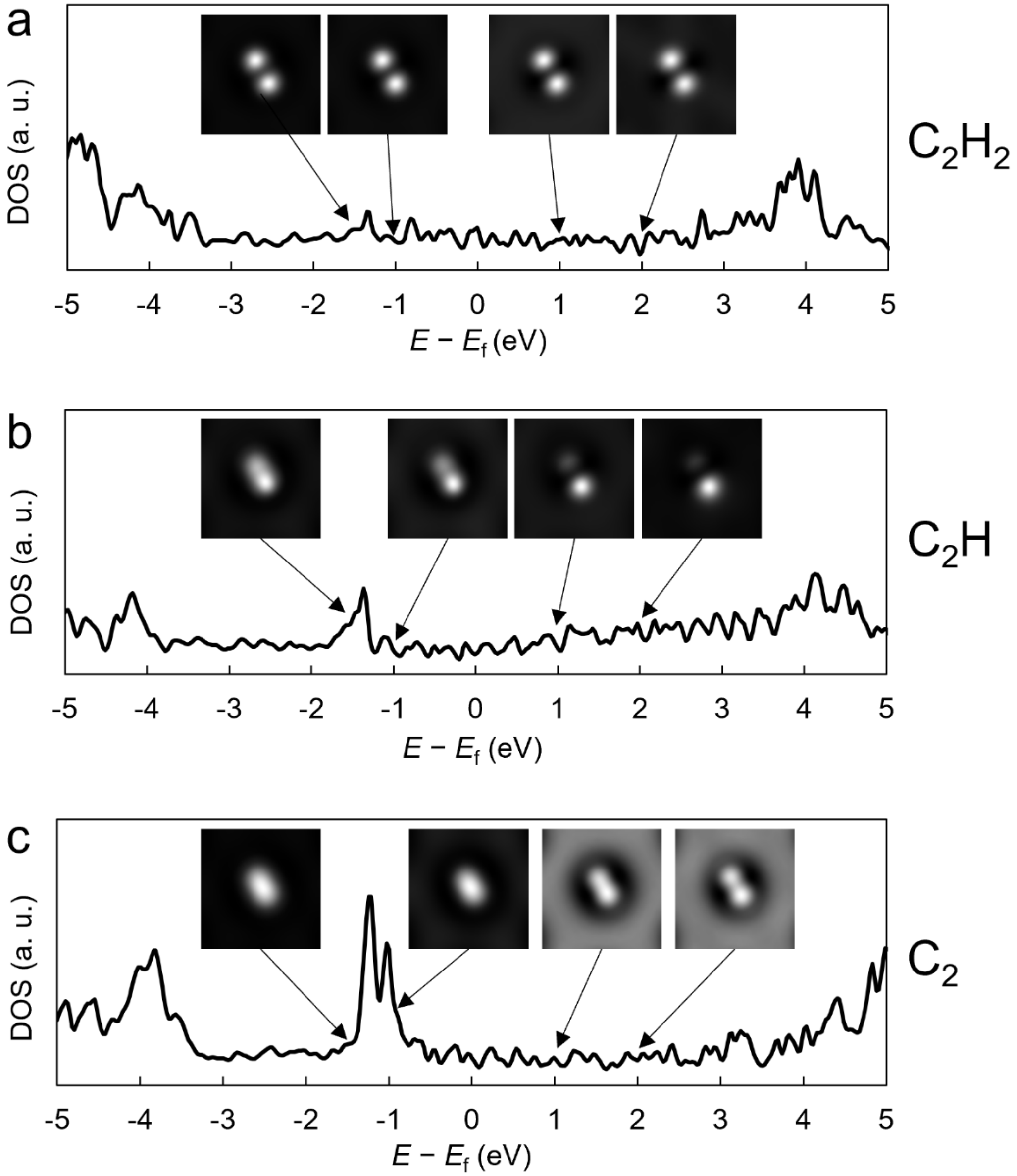

Figure S1. Calculated LDOS and simulated STM images of (a) C_2H_2, (b) C_2H, and (c) C_2 on Cu(111). Each simulated STM image was obtained at energies ($E - E_f$) of 2.0, 1.0, −1.0, and −1.5 eV.

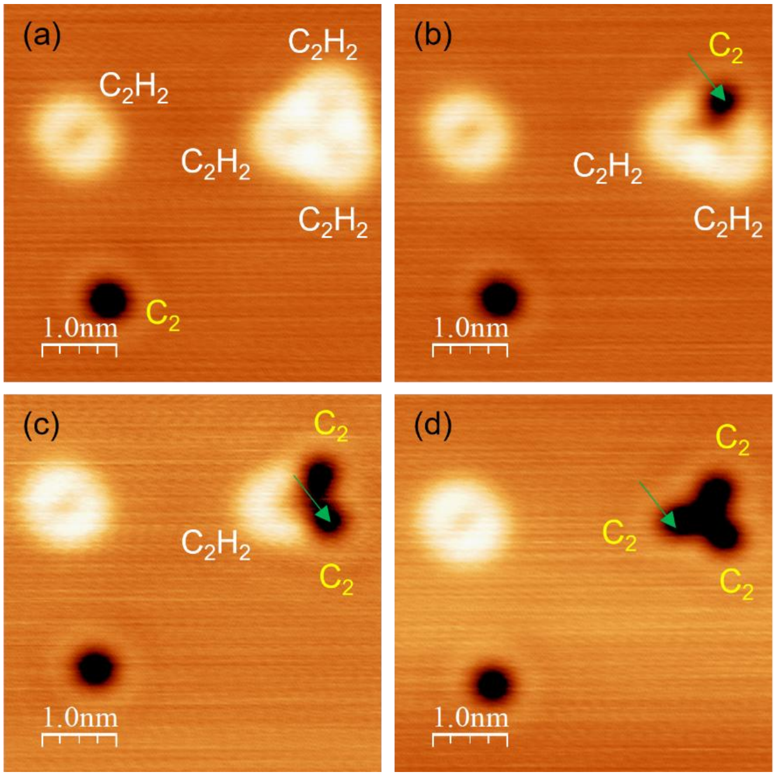

Figure S2. STM images of the reactions of adjacent acetylene molecules one by one (V = 1.5 V, I = 0.5 nA). (a–d) The bright spot in the upper left is a C_2H_2 molecule, while the dark spot on the lower left is a C_2 molecule dehydrogenated from C_2H_2 by applying voltage. Under these scanning conditions, the center of the C_2H_2 bright spot has a height of ~15 pm, and that of the C_2 dark spot has a depth of ~35 pm, relative to the Cu surface. (a) The bright triangular feature on the right consists of three adjacent C_2H_2 molecules. (b–d) A voltage is applied directly above each adjacent C_2H_2 molecule, inducing dehydrogenation one by one to produce C_2 molecules. The green arrows indicate the tip positions where a voltage of 2.8 V was applied.

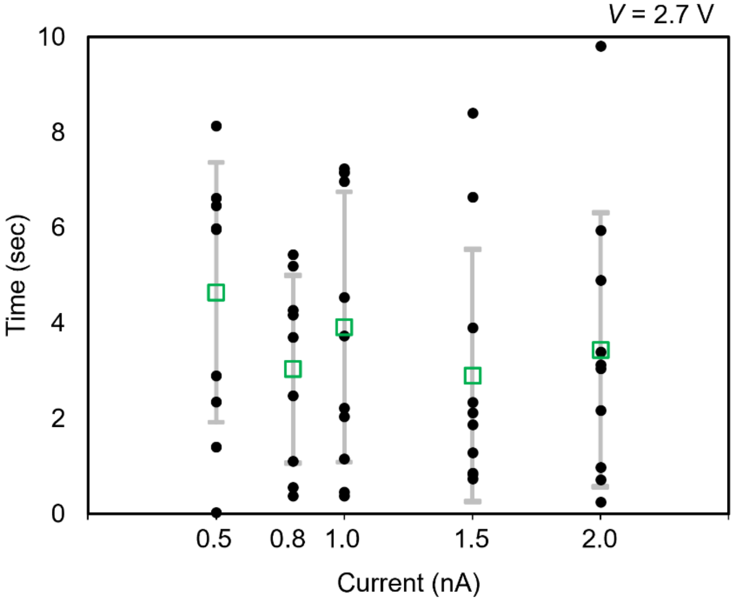

Figure S3. Reaction times (time taken for the current to drop) for 50 acetylene molecules that underwent reaction under a 2.7 V applied voltage (near the reaction threshold) for 10 seconds. Reaction times (vertical axis) were recorded for 9–11 molecules at current values of 0.5, 0.8, 1.0, 1.5, and 2.0 nA (horizontal axis), respectively. Green squares represent the mean reaction times, and grey error bars indicate the standard deviations. The data shows negligible correlation between reaction time and current values.

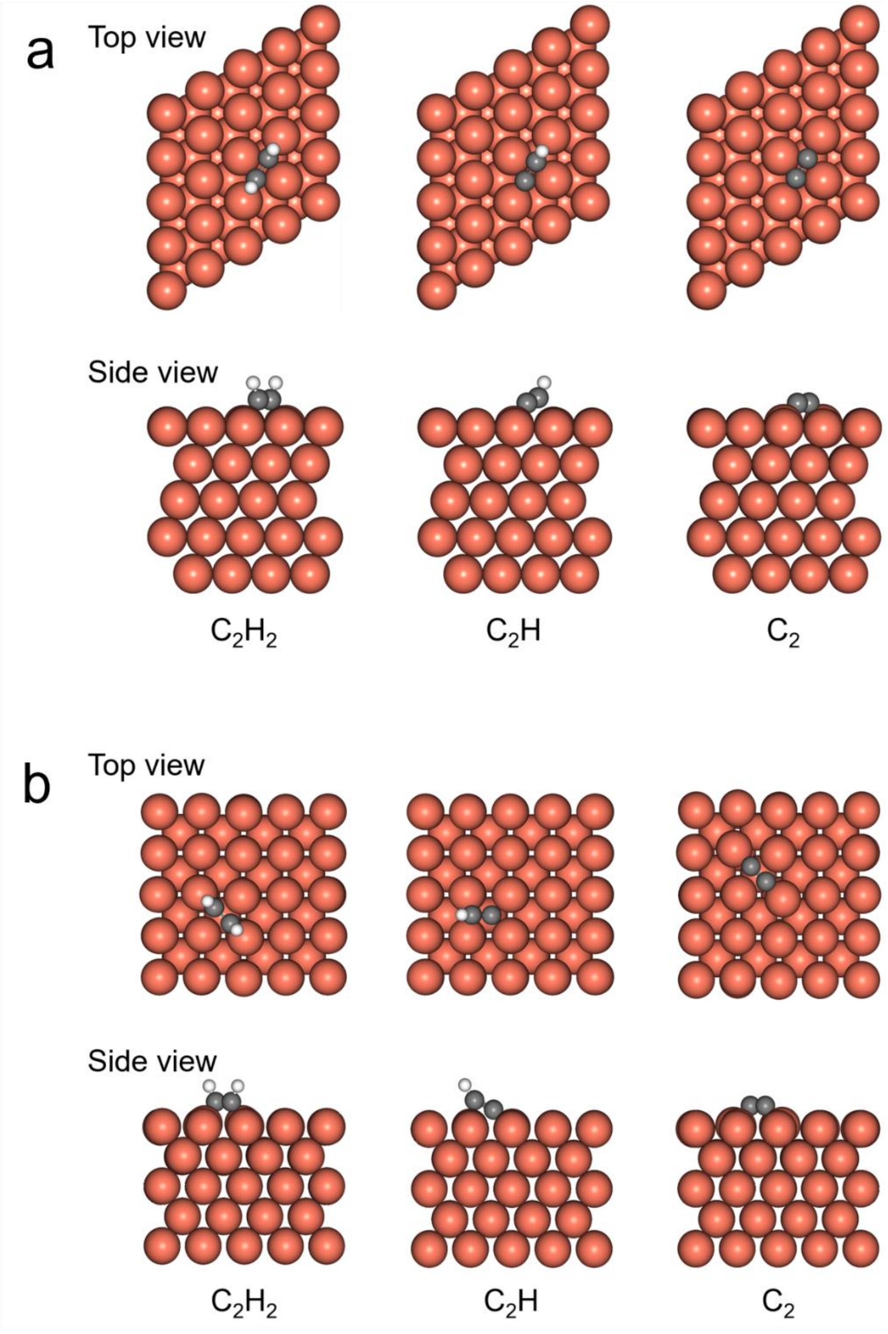

Figure S4. Optimized structures of C_2H_2, C_2H, and C_2 on (a) Cu(111) and (b) Cu(100) surfaces by DFT calculations.

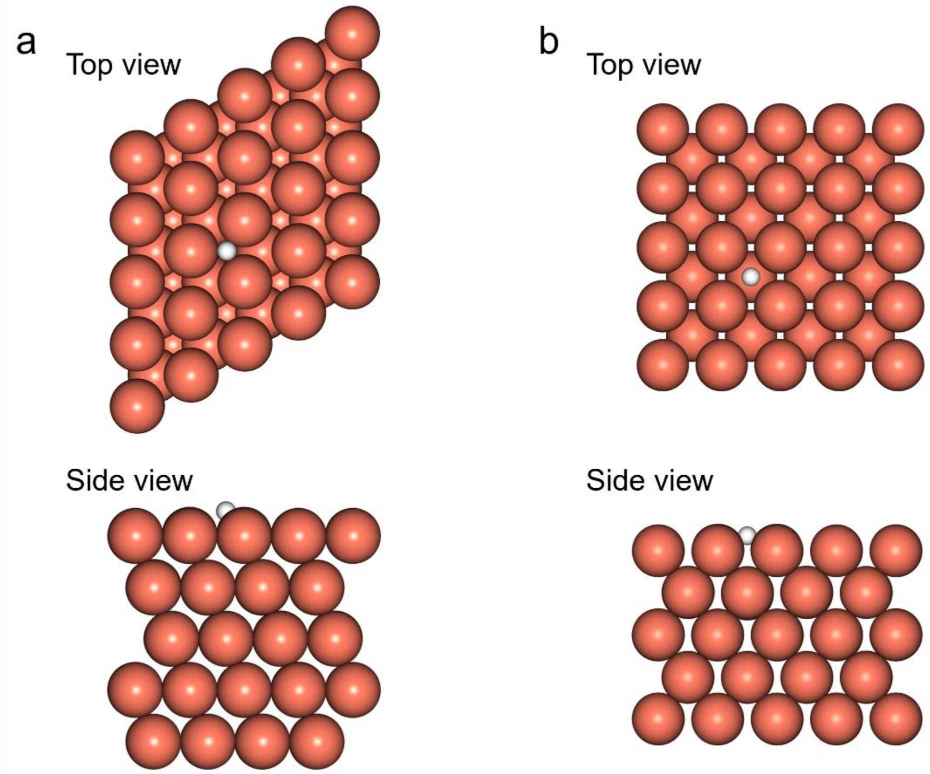

Figure S5. Optimized structures of a hydrogen atom on (a) Cu(111) and (b) Cu(100) by DFT calculations.

References

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