

SUPPLEMENTARY INFORMATION

FOR

Frustrated amino functional group coupling with electric field makes CO₂ activation easier

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Computational method

All calculations were performed using the Vienna ab initio simulation package (VASP) with the projector augmented wave formalism.[1] The electron-ion interactions were described by projected augmented wave (PAW) method with a kinetic energy cutoff of 420 eV. To correctly depict interaction caused by polarization and dispersion, van der Waals interactions was included in the D2 method of Grimme.

During the geometry optimization, the bottom two atomic layers was fixed and the remaining atoms were relaxed using a conjugate gradient method until the Hellmann-Feynman force on every atom could be smaller than 0.02 eV/Å. And the total energy converged to 1e-5 eV and the Brillouin zone was sampled with a 3×3×1 Monkhorst-Pack k point grid. The smearing method of second Methfessel-Paxton (MP) was applied with sigma parameter of 0.1 eV to determine how the partial occupancies.

The external electric field is actualized by adding an artificial dipole sheet defined by Neugebauer and Scheffler, which allows us to specify the direction and intensity of an electric field ranging from -0.6 V/Å to 0.6 V/Å perpendicular to the slab, i.e., along z axis. The direction of applied electric field was perpendicular to the Cu(111), and the upward (downward) direction was defined as a positive (negative) one. Dipole corrections was turned on to avoid interactions between the periodically repeated images.

The adsorption energy of a molecular CO₂ interaction with Cu(111) and CH₃NH₂ is defined as follows:

$$E_b = E_{\text{(Cu+CO}_2\text{+CH}_3\text{NH}_2\text{)}} - E_{\text{(Cu+CH}_3\text{NH}_2\text{)}} - E_{\text{CO}_2}$$

where $E_{\text{(Cu+CO}_2\text{+CH}_3\text{NH}_2\text{)}}$ denote the energy of the optimized configurations of CO₂ in Cu(111) with CH₃NH₂ under electric field, $E_{\text{(Cu+CH}_3\text{NH}_2\text{)}}$ indicates the energy of the stable energy of Cu(111) with CH₃NH₂ under corresponding electric field, E_{CO_2} represents the energy of the stable energy of CO₂ in the gas phase.

The charge density difference ($\nabla\rho$), was obtained by subtracting electron density of CO₂ and Cu-CH₃NH₂ in standalone state from the whole system:

$$\nabla\rho = \rho(\text{Cu-CH}_3\text{NH}_2\text{-CO}_2) - \rho(\text{Cu-CH}_3\text{NH}_2) - \rho(\text{CO}_2)$$

Bader program[2] and PSI4 software [3] were used to analyze charge transfer and decompose energy contributions.

Stable structures under CH_3NH_2 at flexible altitude and electric field

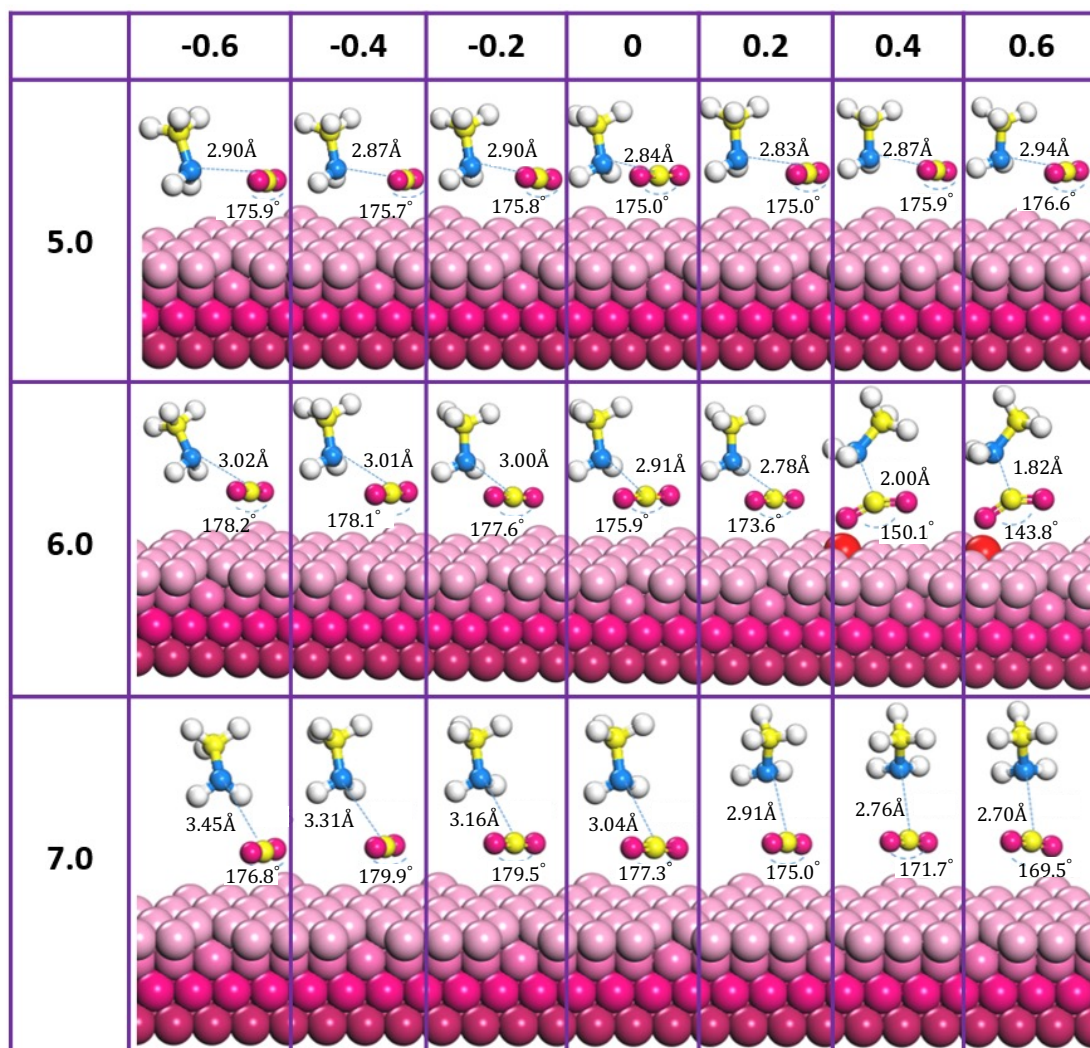


Figure SI-A. Optimized configurations of CO_2 adsorbed on microenvironments of CH_3NH_2 hanging at three heights 5.0 Å, 6.0 Å, 7.0 Å above $\text{Cu}(\text{II})$ with flexible electric field ranging from $-0.6\text{V}/\text{Å}$ to $0.6\text{V}/\text{Å}$. unit is angstrom for distance and degree for angle.

PSI energy decomposition analysis

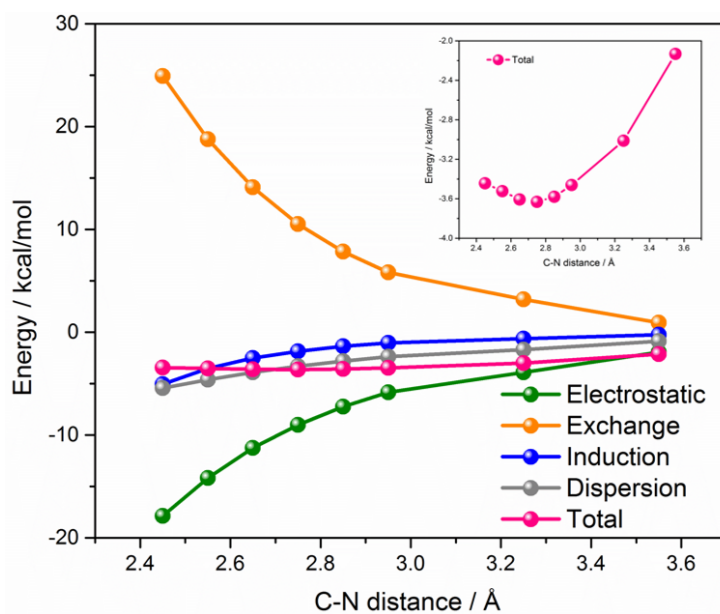


Figure SI-B. Energy decomposition analysis as C-N distance changes.

Density of state

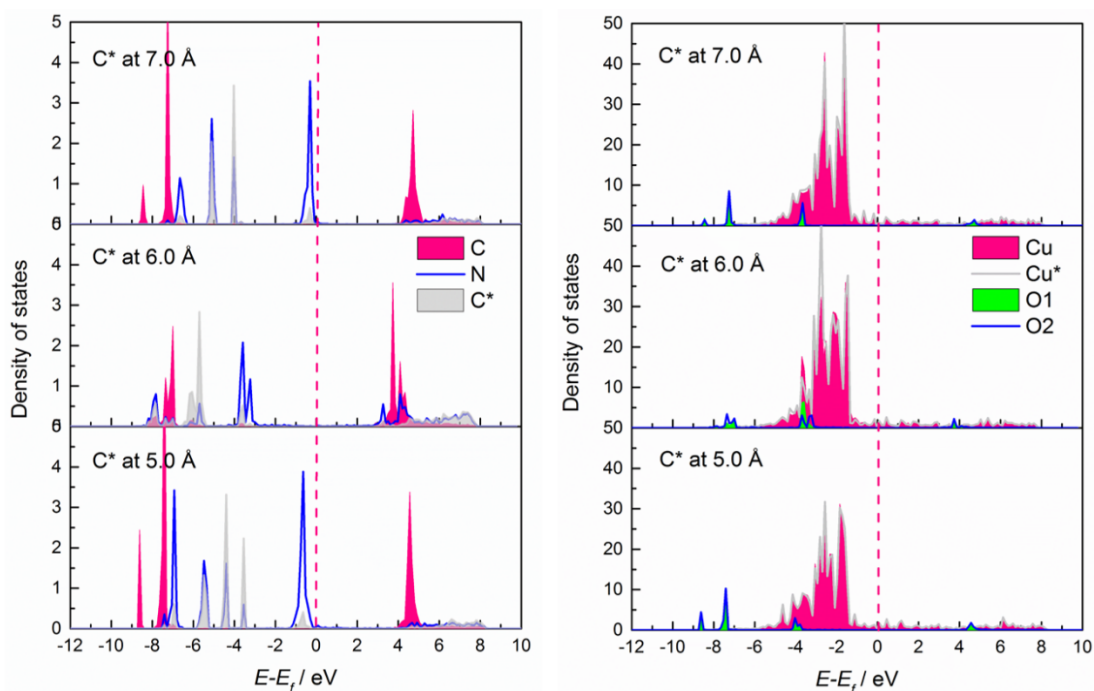


Figure SI-C. left: Projected density of states of C in CO₂, C and N in CH₃NH₂ of optimized configurations of three attitudes CH₃NH₂ above Cu(111) under 0.6 V/Å. right: Projected density of states of Cu and O at the same condition as figure a, where O1 is the close oxygen atoms in CO₂ to Cu(111), O2 is another oxygen atom in CO₂. Cu is the closest copper atom to O1, Cu* is a reference copper on the surface without direct interaction with CO₂.

PH₂ series of functional groups

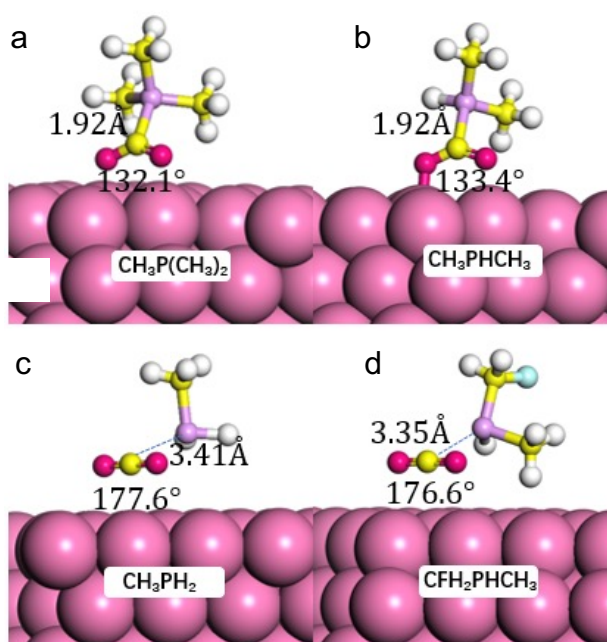


Figure SI-D. Optimized configurations of CO₂ under CH₃PH₂ series chemical groups including electron-donor groups CH₃P(CH₃)₂(a), CH₃PHCH₃(b) and electron-acceptor groups where H in CH₃ was replaced by F(d), hanging 6.0 Å above Cu(111) surface under electric field strength 0.6 V/Å.

OH functional group

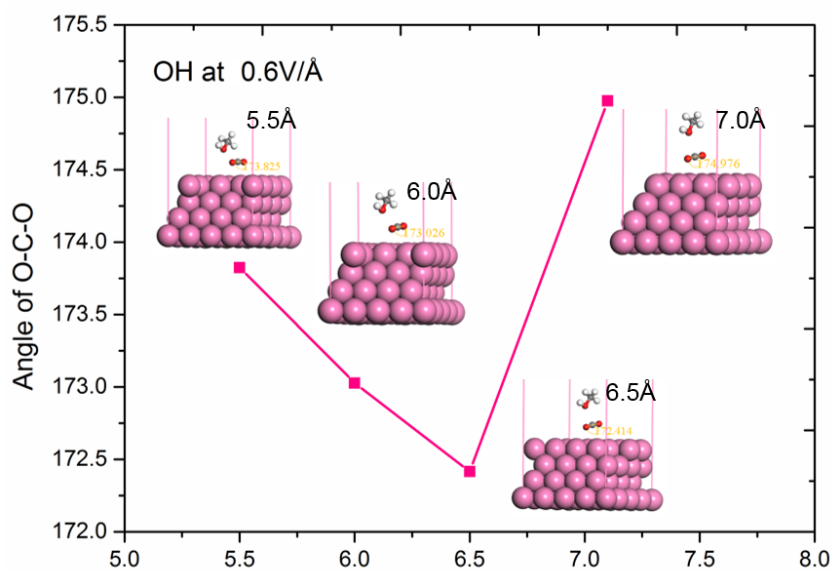


Figure SI-E. Optimized configurations of CO₂ adsorbed on microenvironments of CH₃OH hanging at different height above Cu(111) with 0.6 V/Å electric field.

References

- (1) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical review b* **1999**, *59*, 1758.
- (2) Yu, M.; Trinkle, D. R. Accurate and efficient algorithm for Bader charge integration. *The Journal of chemical physics* **2011**, *134*, 064111
- (3) Parrish, R. M.; Burns, L. A.; Smith, D. G.; Simmonett, A. C.; DePrince III, A. E.; Hohenstein, E. G.; Bozkaya, U.; Sokolov, A. Y.; Di Remigio, R.; Richard, R. M., et al. Psi4 1.1: An open-source electronic structure program emphasizing automation, advanced libraries, and interoperability. *Journal of chemical theory and computation* **2017**, *13*, 3185–3197.