Supplementary Information

Organic Additive for the Selective C_2-Product Formation on Cu(100): A Density Functional Theory Mechanistic Study

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Text S1:

For the first principles calculations 4×3×1 supercell of Cu(100) has been considered with ~15 Å vacuum along the z-direction in order to avoid possible interactions between two periodic images. A 3 × 3 × 1 Γ- kpoint mesh has been considered to sample the Brillouin zone for the modelled systems. The difference in calculated energies considering 3 × 3 × 1 and 5 × 3 × 1 Γ-kpoint mesh were found to be insignificant. To enlarge the electronic wave function**,** plane wave cut-off energy has been set to 470 eV. All the structures have been relaxed until the forces and the electronic energies became < 0.02 eV Å^{-1} and < 10^{-4} eV, respectively. The adsorption energy (E_{ad}) of the intermediates were calculated considering the following equation (1),

$$E_{ad} = E_{slab + adsorbate} - (E_{slab} + E_{adsorbate}) \tag{1}$$

Here, $E_{slab + adsorbate}$, E_{slab} and $E_{adsorbate}$ are the total energy of surface with adsorbed species, single point energy of pristine surface and adsorbate, respectively. The interaction energy (E_{int}) of CO$_2$ with additives are calculated considering the following equation (2),

$$E_{int} = E_{additive + CO_2} - (E_{additive} + E_{CO_2}) \tag{2}$$

Here, $E_{additive + CO_2}$, $E_{additive}$ and $E_{CO_2}$are the calculated single point energies of additive+CO$_2$ considered from optimized structure on the Cu(100) surface, additive and CO$_2$, respectively. The computational hydrogen electrode (CHE) model, proposed by Nørskov and co-workers, is used to calculate the reaction free energy (ΔG) at 0 V (vs reversible hydrogen electrode, RHE).[1,2] The free energy has been calculated considering the following equation (3),

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \tag{3}$$

In equation 2, ΔE defines the total energy difference between the initial and the final states, ΔZPE is the change in zero-point energy, T denotes the temperature and ΔS is the change in entropy for the reaction. For the entropy correction, 300 K temperature has been considered. The zero-point energy can be calculated using the $\sum \frac{1}{2} h v_i$ equation, where h and v_i defines the Planck's constant and the vibrational frequencies of the intermediates, respectively. Hence, all the reaction free energies reported here are corrected for ZPE as well as entropy ($\Delta E + \Delta ZPE + T\Delta S$). Furthermore, all the intermediate adsorptions have been considered stable on the basis of absence of negative vibrational frequencies. The charge density differences (CDD) (ρ_{CDD}) have be calculated following equation 3 and plotted using visualization for electronic and structural analysis (VESTA) software.[3]

$$\rho_{CDD} = \rho^{total} - \sum_i \rho_i^{fragments}$$

Where, ρ^{total} is the total charge density of the surface with additives and $\rho_i^{fragments}$ is the charge density of the individual fragments. Moreover, we have also calculated Bader atomic charges for some of the important intermediates using Henkelman code with the near-grid algorithm refine-edge method.[4,5] The noncovalent interactions (NCI) have been analysed using Multiwfn software and visualized using the VMD program.[6-10] The implicit solvation was calculated using VASPsol, a software package that incorporates solvation into VASP within a self-consistent continuum model.[11,12]

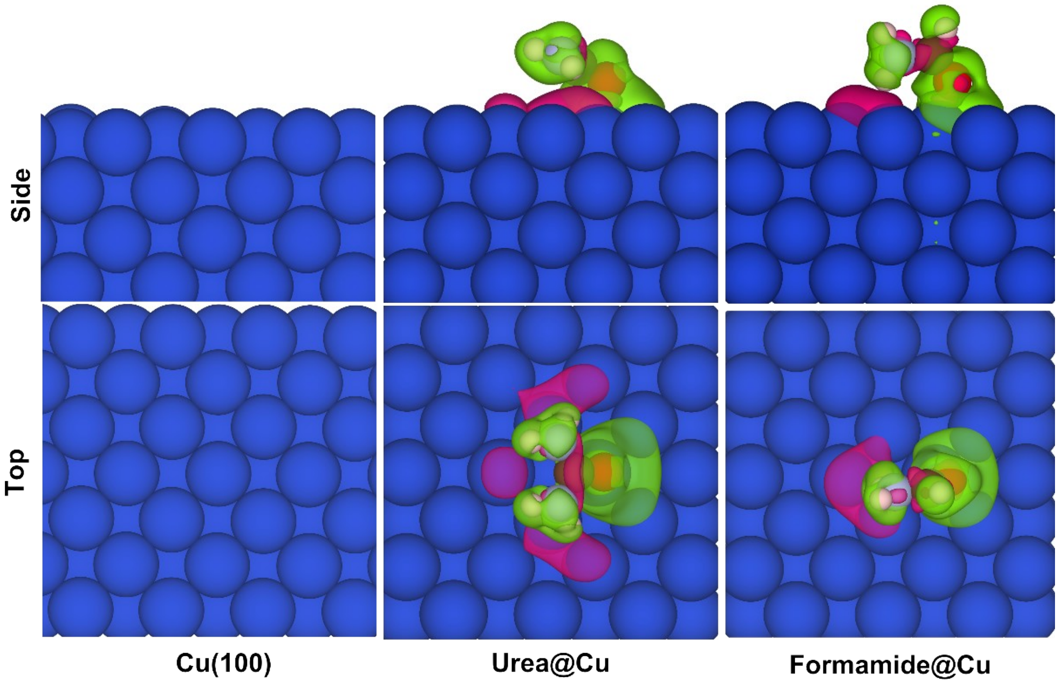

Fig. S1. Charge density difference (CDD) plot of Cu(100), urea@Cu and formamide@Cu surfaces. Here, magenta/green colour indicates electron density accumulation/depletion.

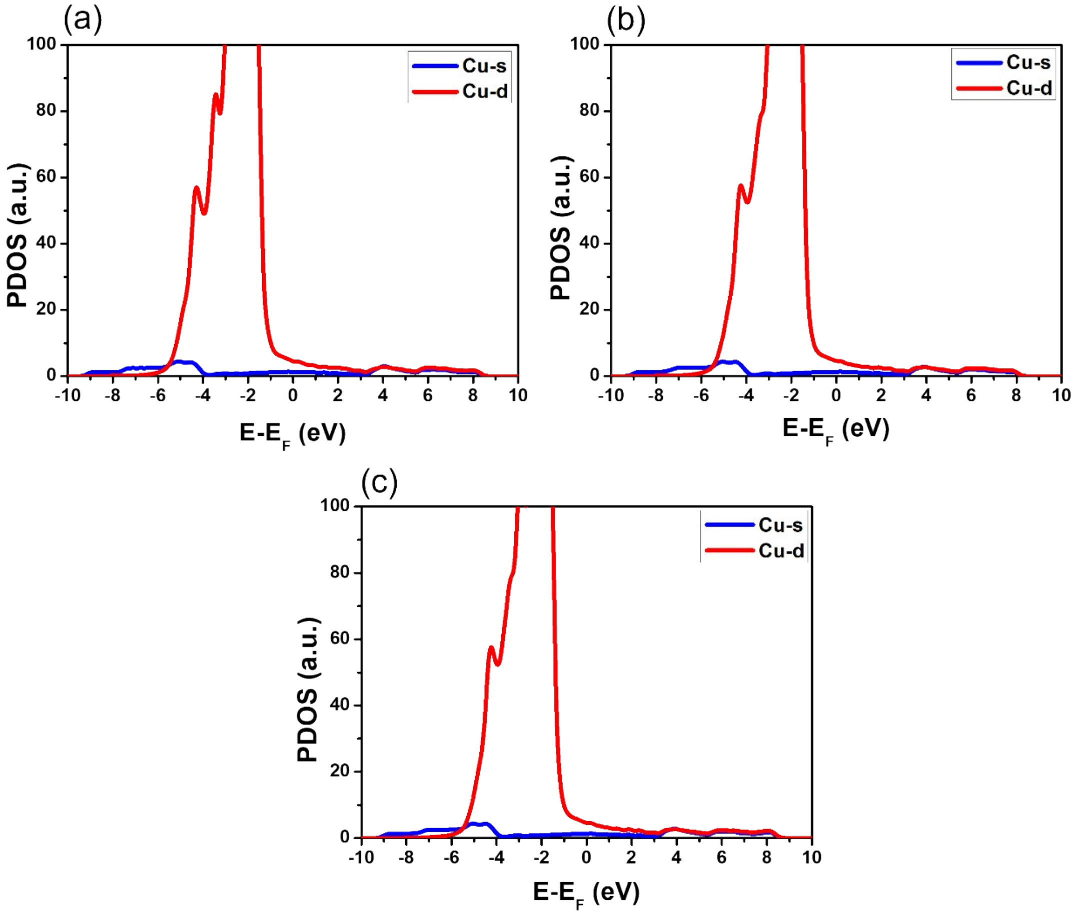

Fig. S2. Projected density of states (PDOS) of d and s orbitals of Cu on (a) Cu(100), (b) formamide@Cu and (c) urea@Cu surfaces.

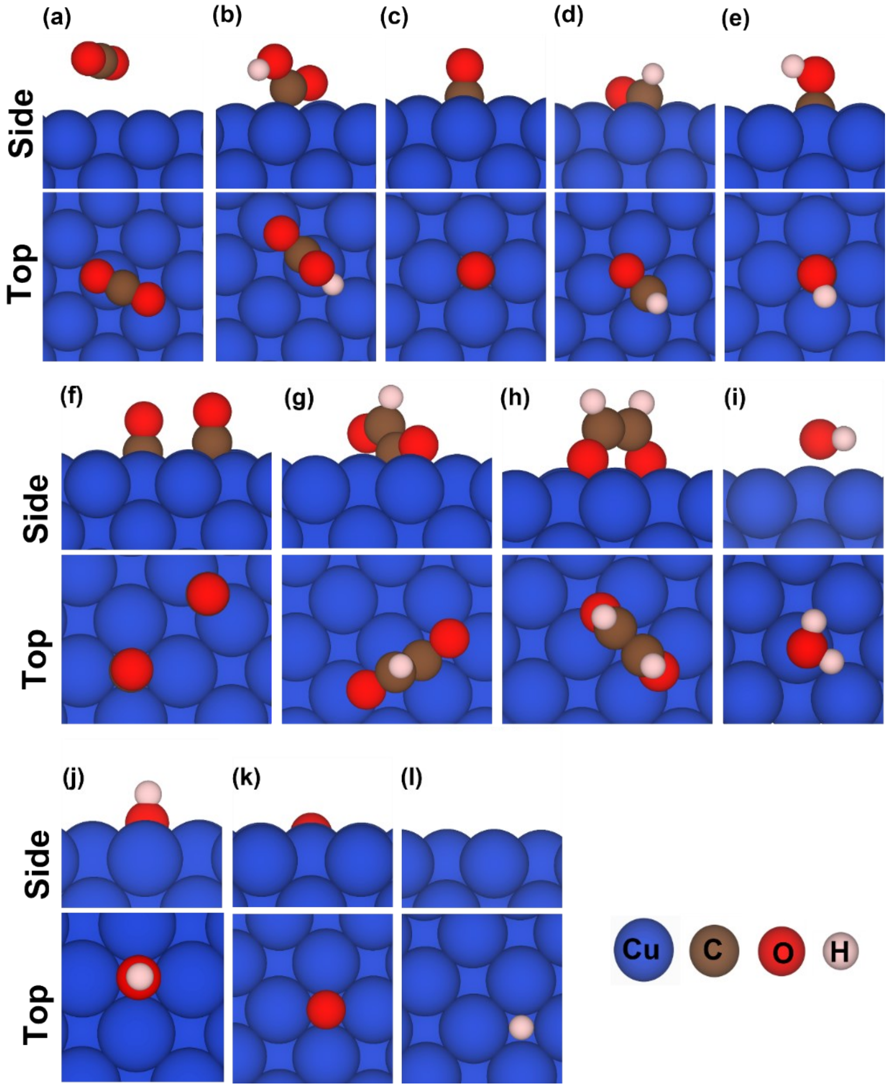

Fig. S3. Adsorption patterns of the considered CO_2 hydrogenation reaction intermediates on the Cu(100) surface: (a) $*CO_2$, (b) *COOH, (c) *CO, (d) *CHO (e) *COH, (f) *CO-*CO, (g) *CO-*CHO, (h) *CHO-*CHO, (i) $*H_2O$, (j) *OH, (k) *O and (l) *H.

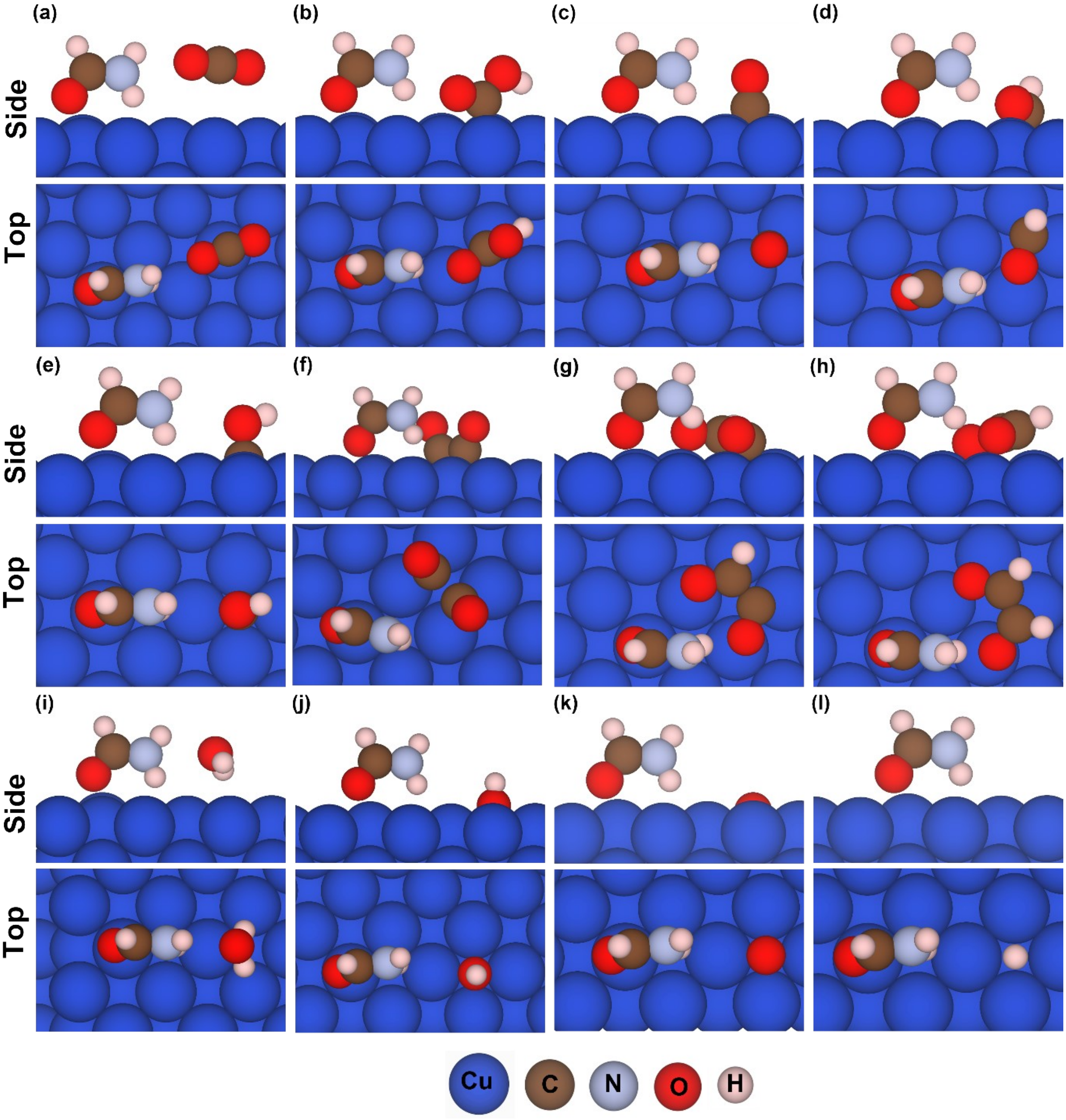

Fig. S4. Adsorption patterns of the considered CO_2 hydrogenation reaction intermediates on the formamide@Cu(100) surface: (a) $*CO_2$, (b) *COOH, (c) *CO, (d) *CHO (e) *COH, (f) *CO-*CO, (g) *CO-*CHO, (h) *CHO-*CHO, (i) $*H_2O$, (j) *OH, (k) *O and (l) *H.

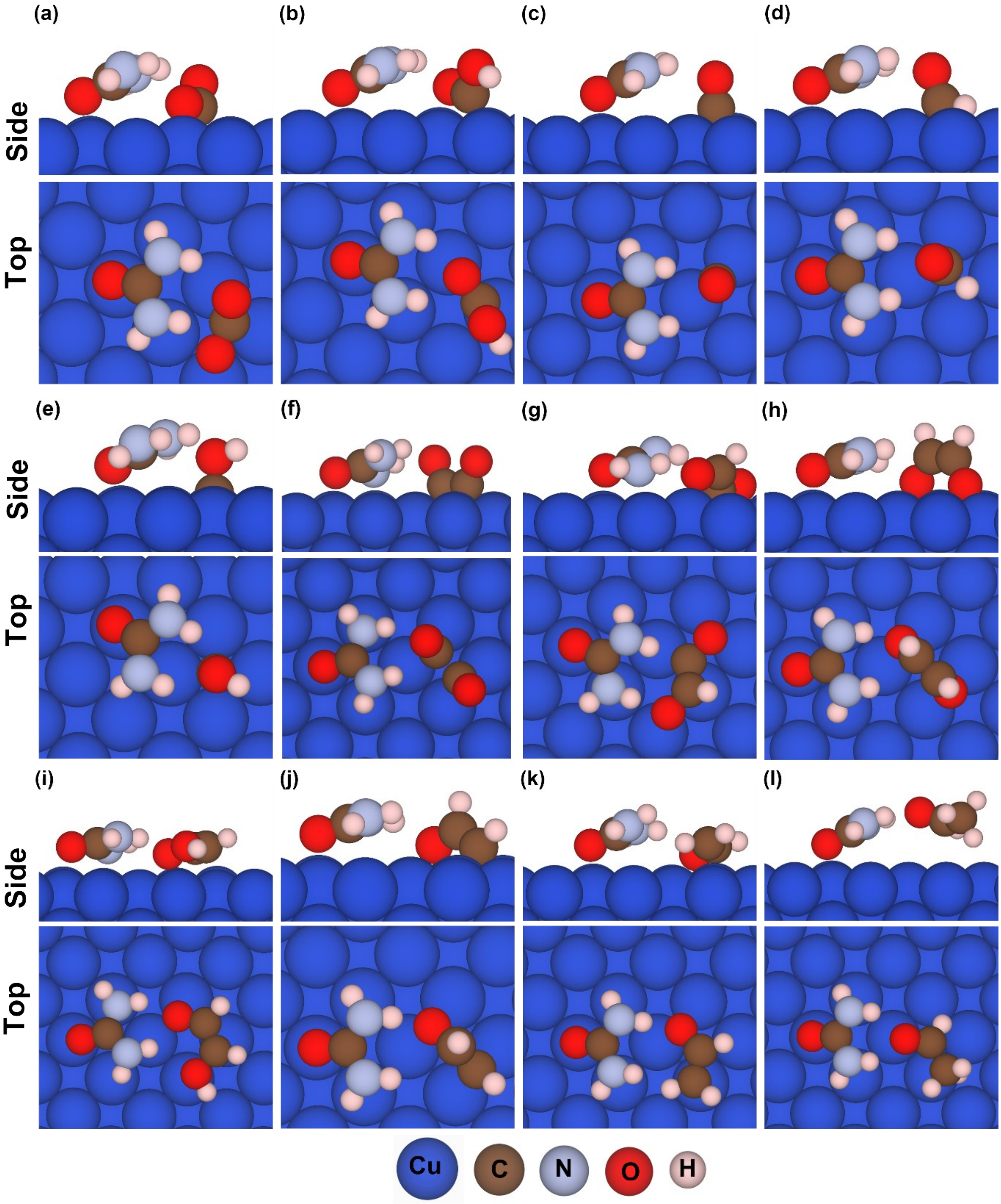

Fig. S5. Adsorption patterns of the considered CO_2 hydrogenation reaction intermediates on the urea@Cu(100) surface: (a) $*CO_2$, (b) *COOH, (c) *CO, (d) *CHO (e) *COH, (f) *CO-*CO, (g) *CO-*CHO, (h) *CHO-*CHO, (i) *CHO-*CHOH, (j) *CHCHO, (k) $*CH_2CHO$ and (l) $*CH_3CHO$.

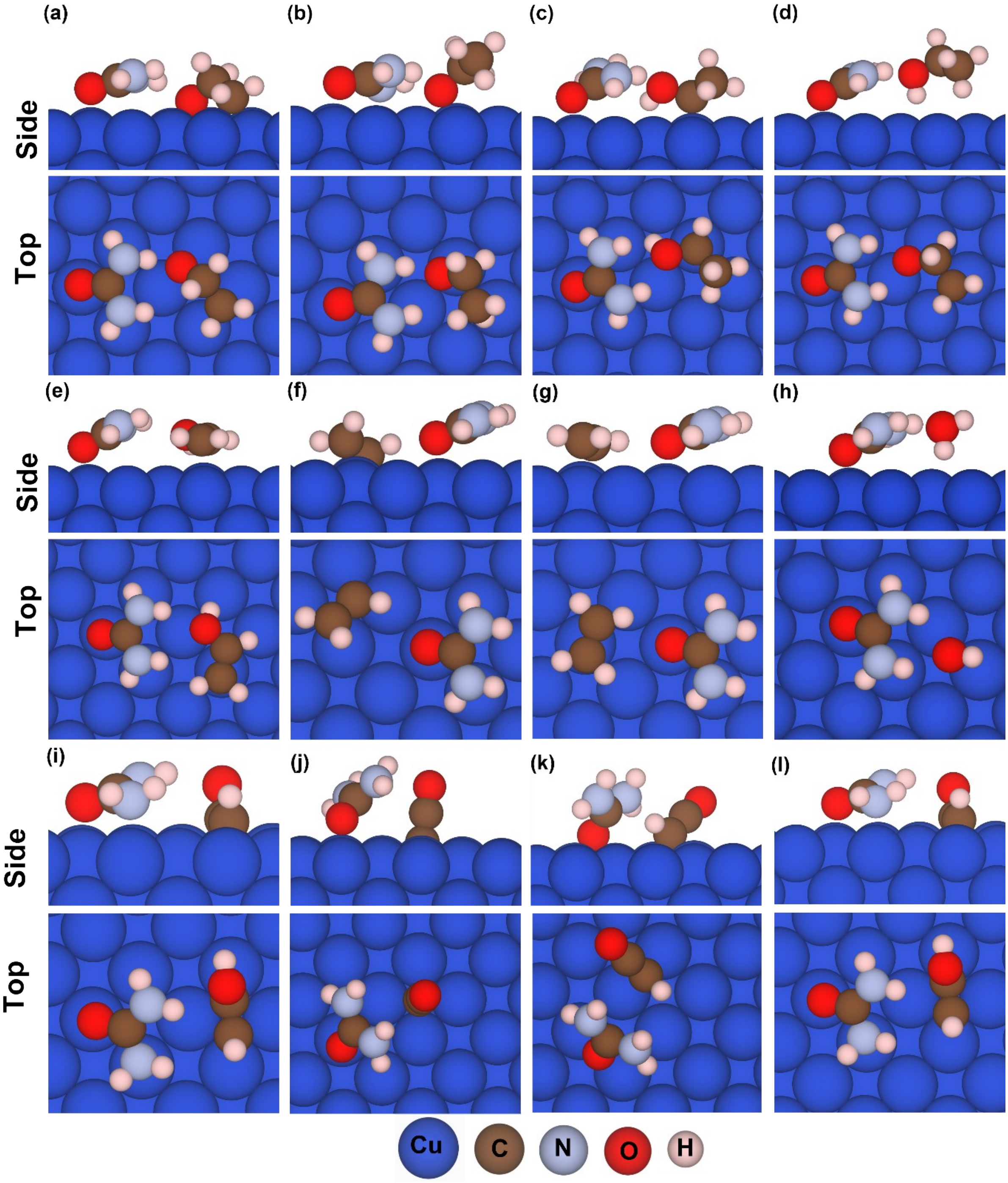

Fig. S6. Adsorption patterns of the considered CO_2 hydrogenation reaction intermediates on the urea@Cu surface: (a) $*CH_2CH_2O$, (b) $*CH_3CH_2O$, (c) $*CH_3CHOH$, (d) $*CH_3CH_2OH$, (e) $*CH_2CHOH$, (f) $*CH_2CH$ and (g) $*CH_2CH_2$, (h) $*H_2O$, (i) $*COCOH$, (j) $*CCO$, (k) $*CHCO$ and (l) $*CHCOH$.

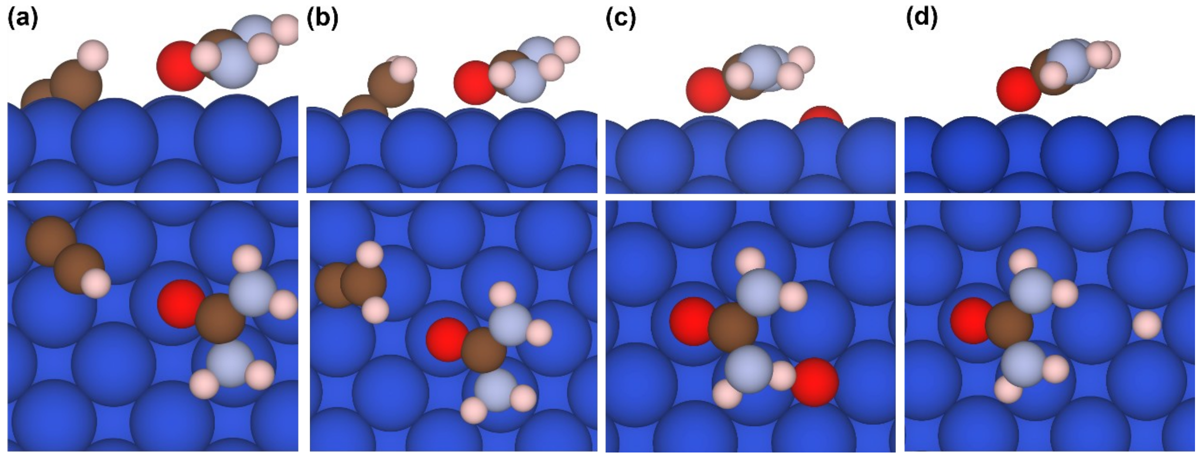

Fig. S7. Adsorption patterns of the considered CO_2 hydrogenation reaction intermediates on the urea@Cu surface: (a) *CCH, (b) *CCH_2, (c) *O and (d) *H.

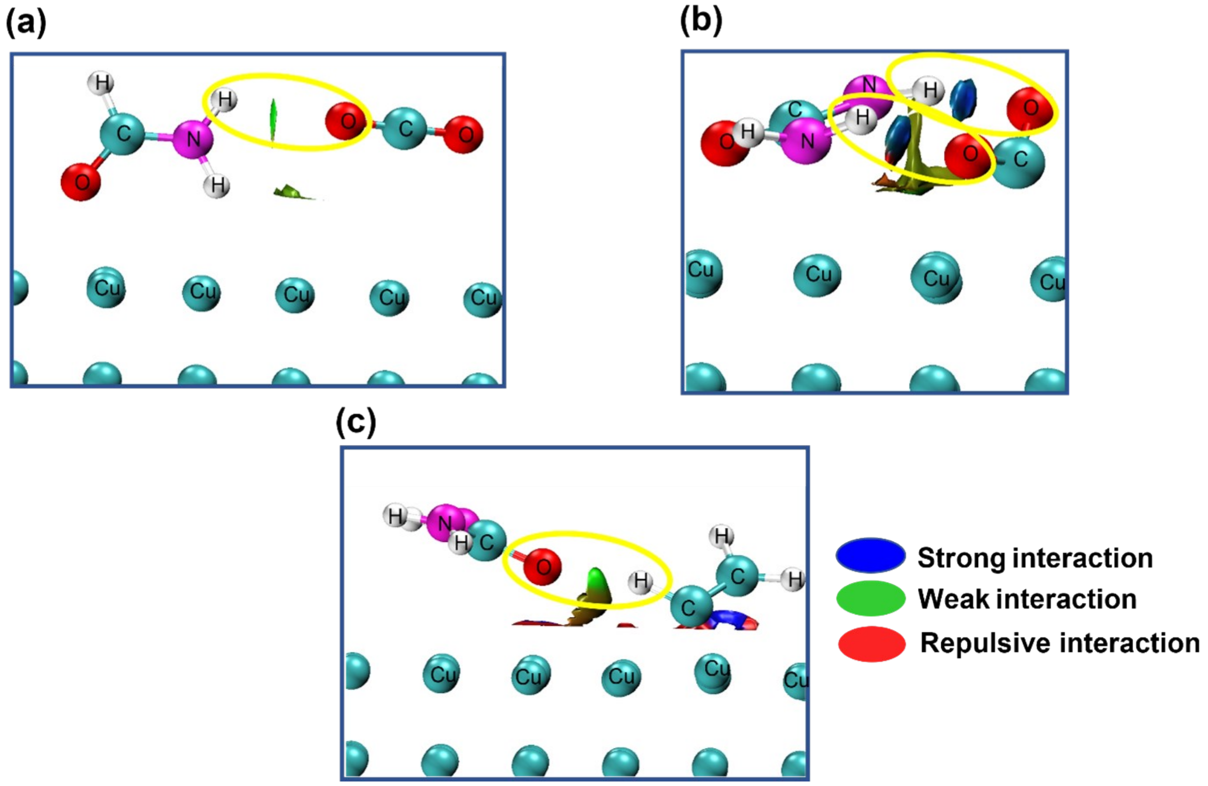

Fig. S8. Non-covalent interactions (NCI) plot of (a) CO_2 on formamide@Cu(100) (b) CO_2 on urea@Cu(100) and (c) CH_2CH on urea@Cu(100) surfaces.

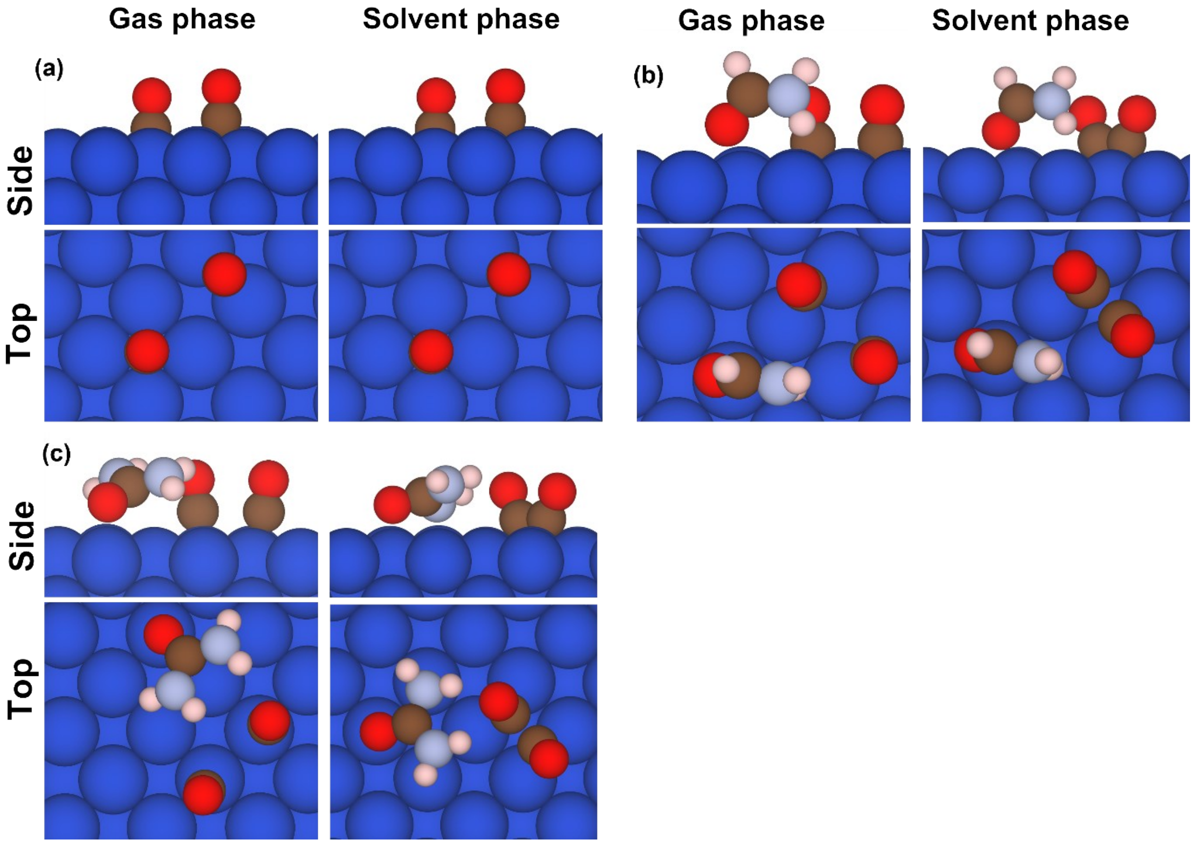

Fig. S9. Adsorption patterns of *CO-*CO intermediate in gas and solvent phase on (a) Cu(100) surface (b) formamide@Cu (c) urea@Cu surface.

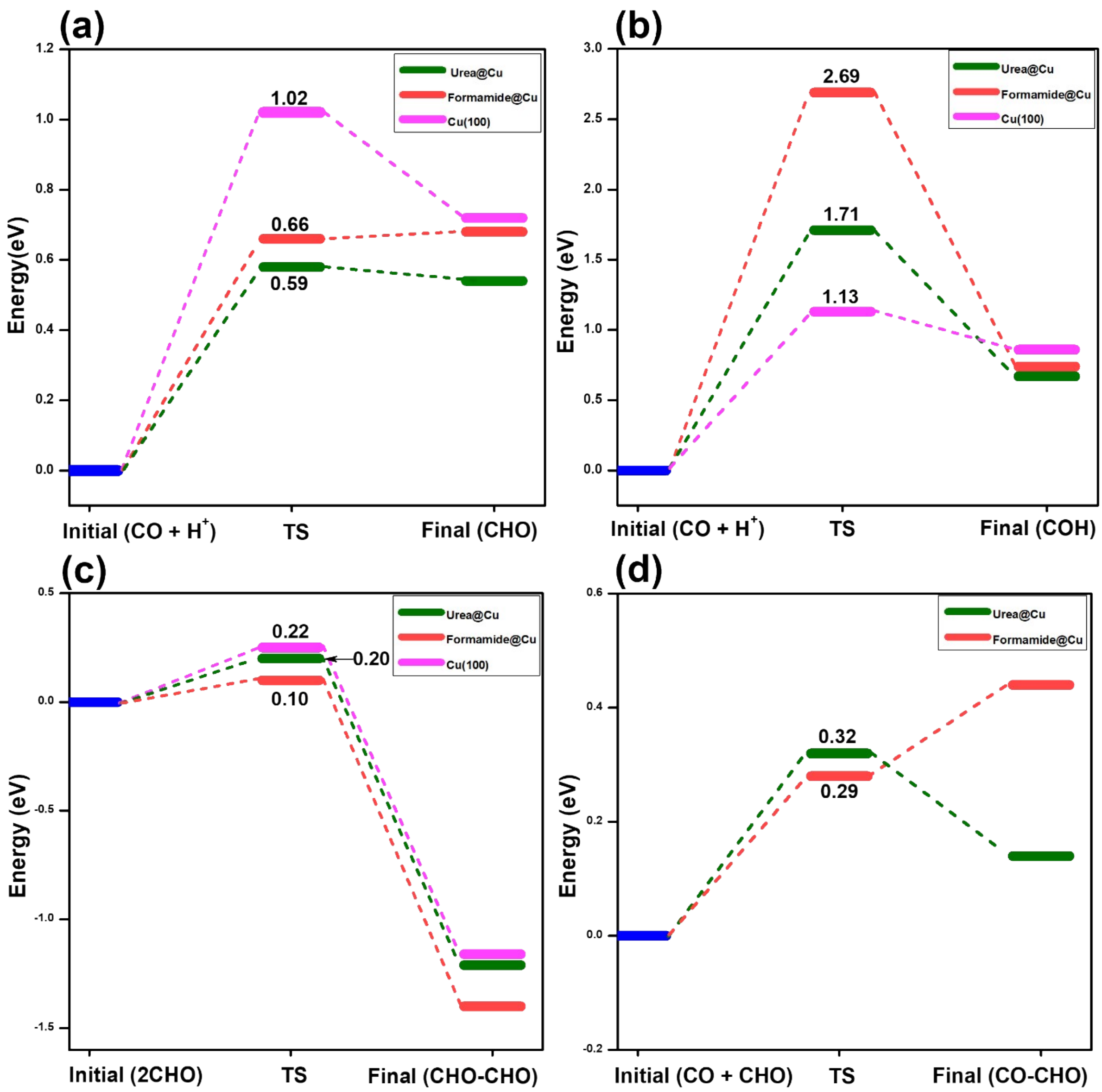

Fig. S10. Kinetic barrier for the formation of (a) *CHO, (b) *COH, (c) *CHO-*CHO and (d) *CO-*CHO on all the considered surfaces in gas phase. All the energies are in eV.

Table S1. Adsorption energies (eV) of all the intermediate for the formation of ethanol and ethylene on the urea@Cu(100) surface. The values in bracket represent the calculated adsorption energy in solvent medium.

Adsorbate	Urea@Cu eV	Adsorbate	Urea@Cu eV
*CHOHCHO	- 2.84 (- 2.49)	*COCOH	- 5.70 (- 5.45)
*CHCHO	- 5.18 (- 5.72)	*CCO	- 6.30 (- 5.96)
*CH_2CHO	- 2.94 (- 2.92)	*CHCO	- 3.53 (- 3.47)
*CH_3CHO	- 0.92 (-0.62)	*CHCOH	- 6.10 (-5.79)
*CH_3CHOH	- 2.09 (- 2.01)	*CCH_2	- 3.91 (- 3.71)
*CH_2CH_2O	- 5.21 (- 5.49)	*CH_3CH_2OH	- 1.04 (- 0.60)
*CH_3CH_2O	- 3.17 (- 3.11)	*CH_2CH	- 3.12 (- 3.55)
*CH_2CHOH	- 1.14 (- 0.95)	*CH_2CH_2	- 1.09 (- 1.28)

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