Supporting Information

Computational investigation of UiO-66 confinement effect on copper clusters: initial hydrogenation of CO_2

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S1. CO_2 hydrogenation

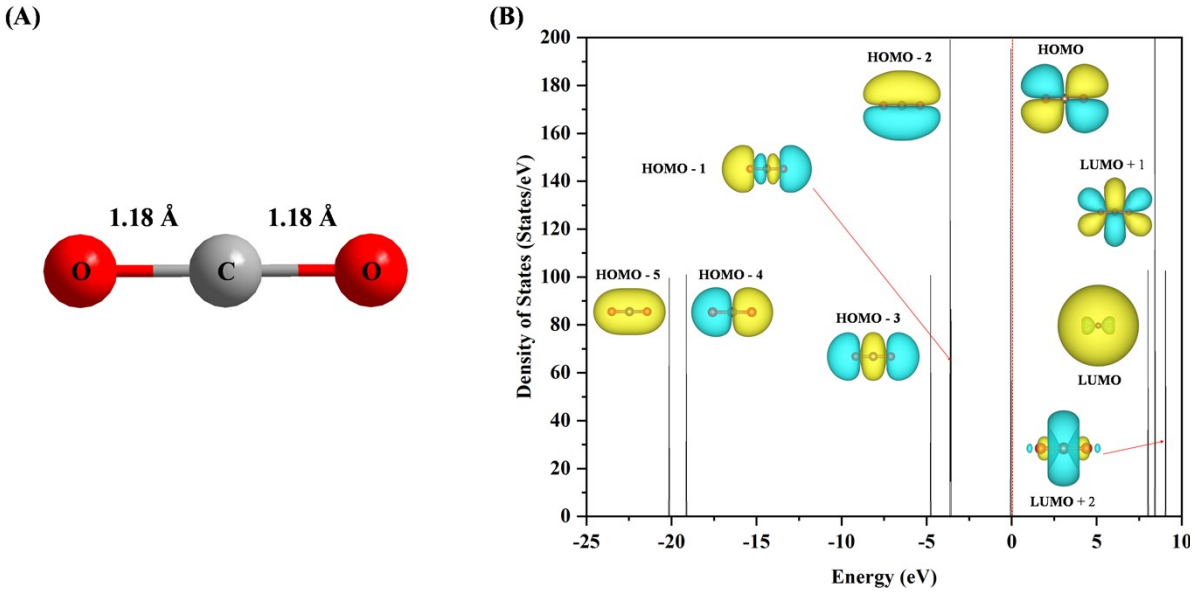

Figure S1. The (A) optimized structure with key bond distance in Å and (B) density of states (DOS) of CO_2 in gas phase.

Table S1. Adsorption energy of H* on catalyst surface ΔE_H obtained using equation: $\Delta E_H = E - E_{catalyst} - E_H$, where E, $E_{catalyst}$ and E_H are electronic energies of adsorption system, catalyst and gas-phase H atom, as well as d-band center (ε_d) of Cu_8, Cu_{16}, Cu_8@UiO-66 and Cu_{16}@UiO-66.

Catalyst	Cu_8	Cu_{16}	Cu_8@UiO-66	Cu_{16}@UiO-66
ΔE_H (kcal mol^{-1})	-47.01	-57.52	-61.42	-63.70
ε_d (eV)	-1.26	-1.88	-1.86	-1.99

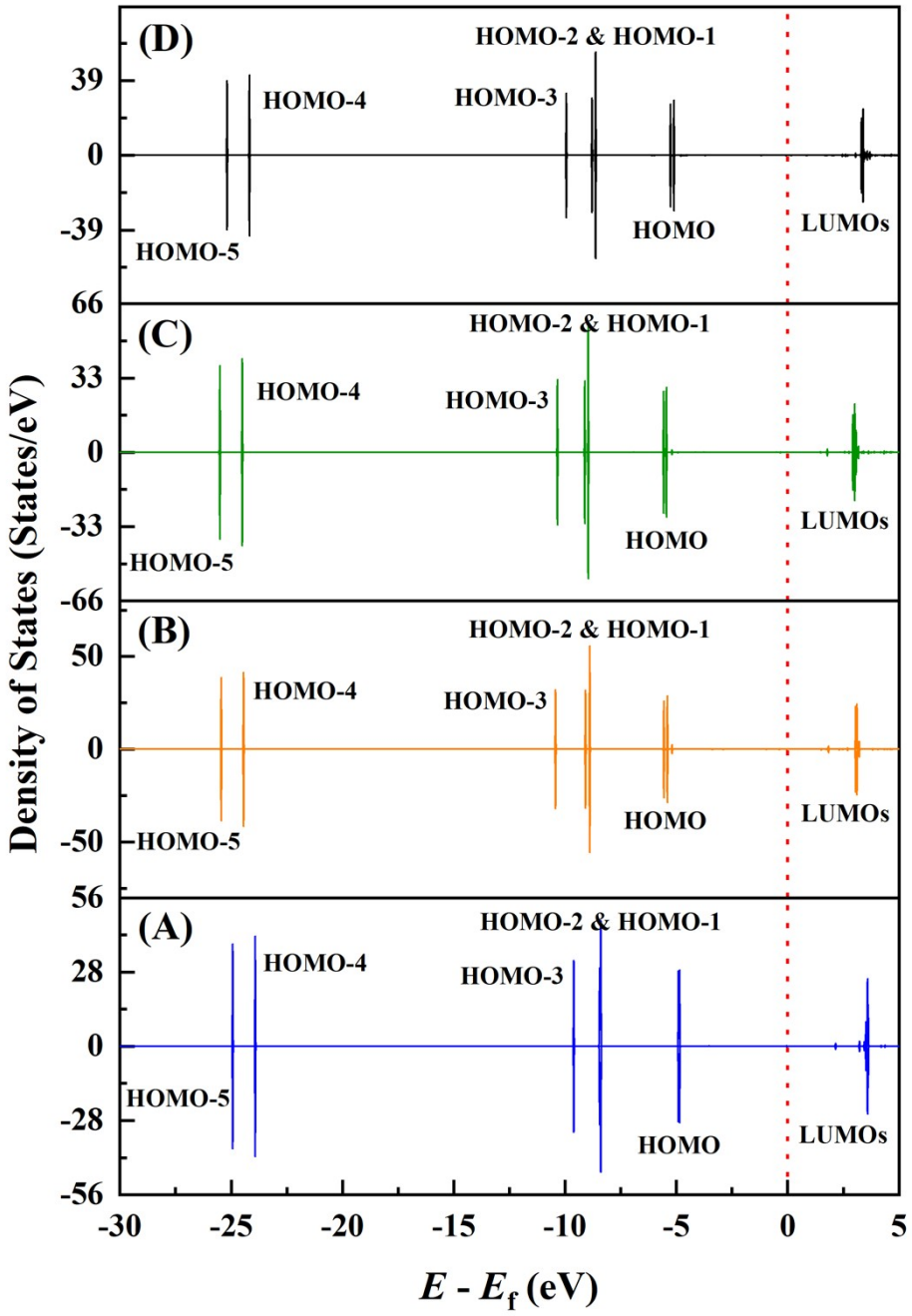

Figure S2. The density of states (DOS) of CO_2 on non-confined (A) Cu_4, (B) Cu_8, (C) Cu_{16} and (D) Cu_{32}.

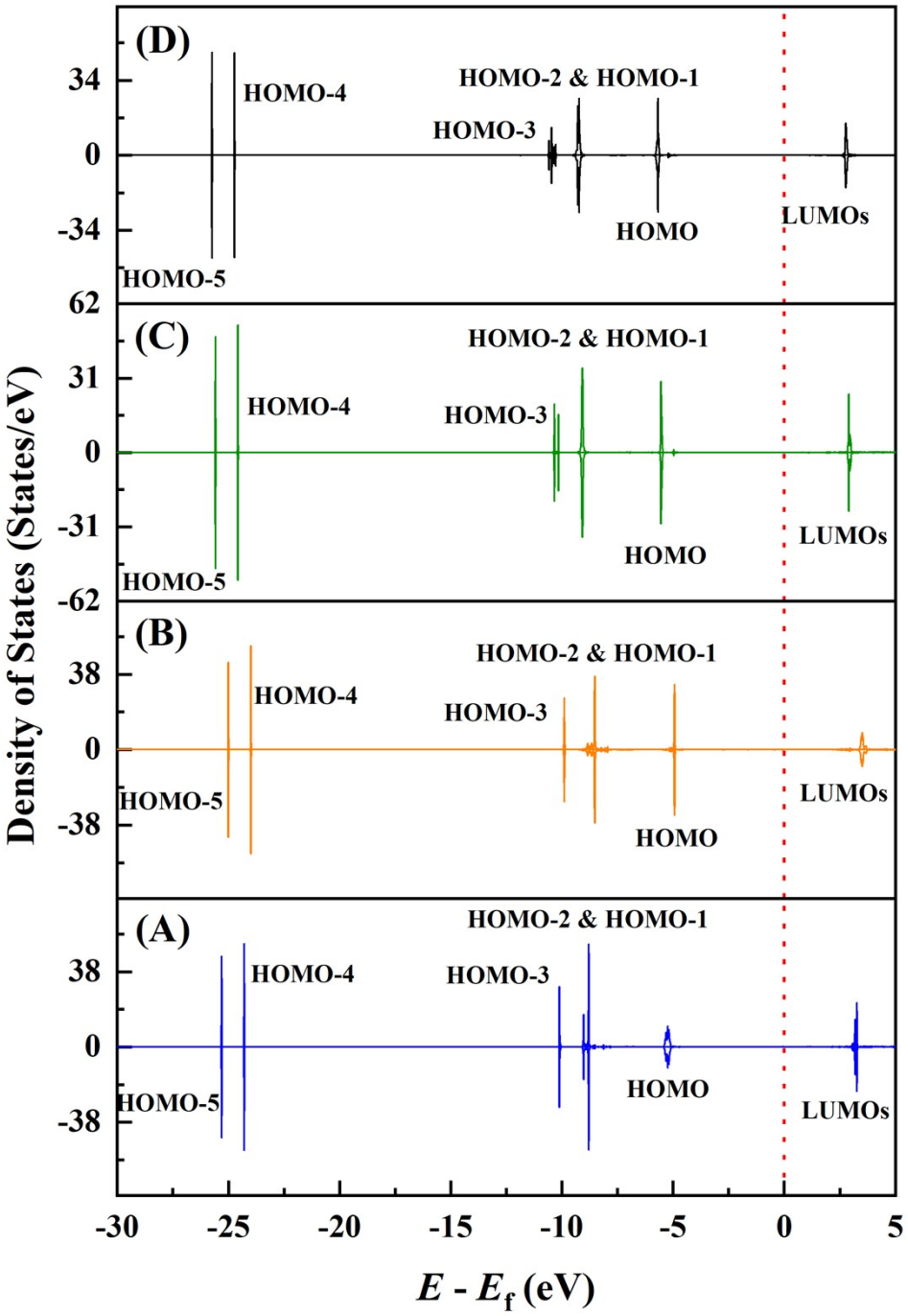

Figure S3. The density of states (DOS) of CO_2 on UiO-66-confined (A) Cu_4, (B) Cu_8, (C) Cu_{16} and (D) Cu_{32}.

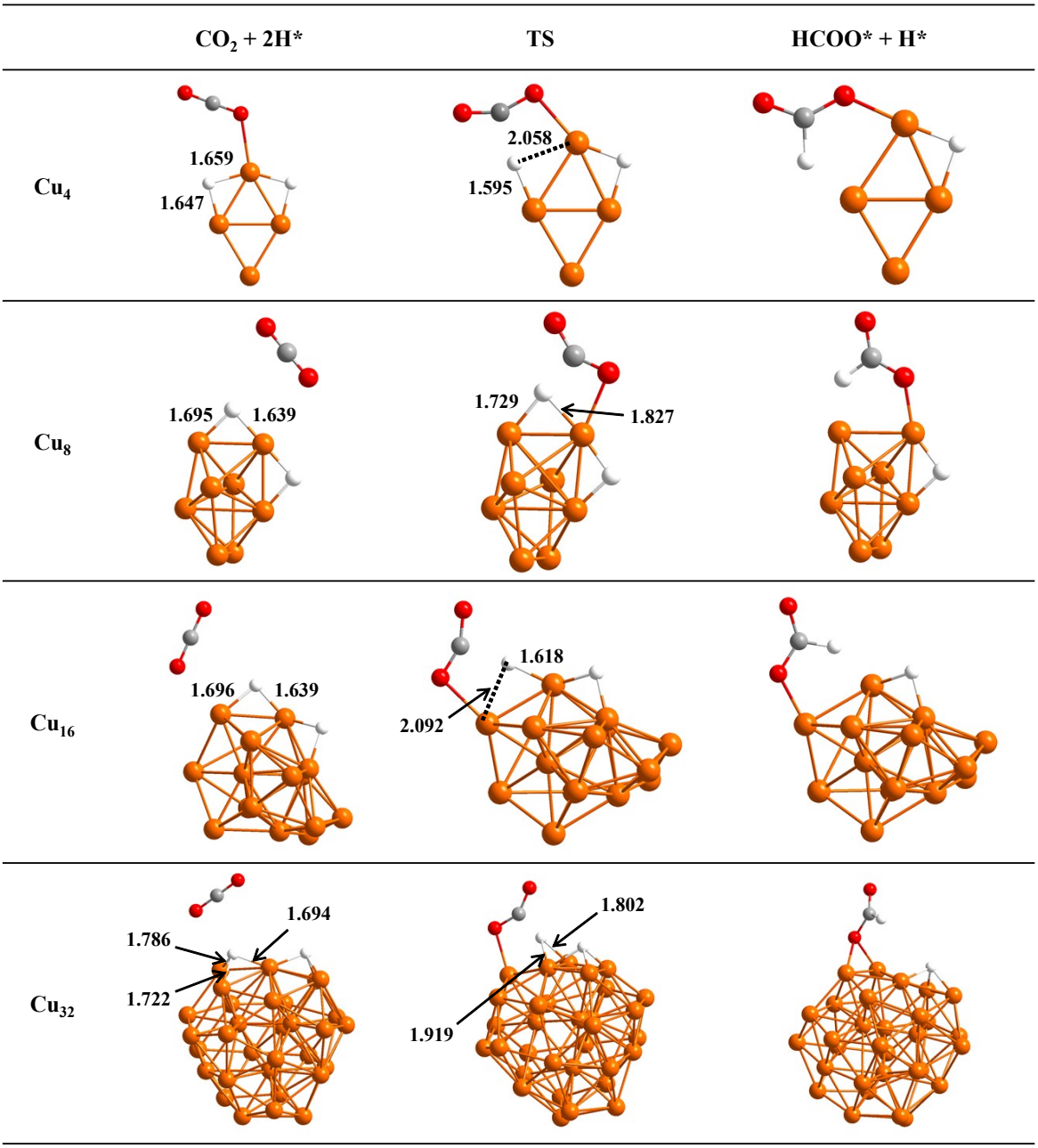

Figure S4. The optimized structures of CO_2 hydrogenation on non-confined Cu_n (n = 4, 8, 16, 32) with key bond distance (Å), where H C, O and Cu are in white, grey, red and orange, respectively.

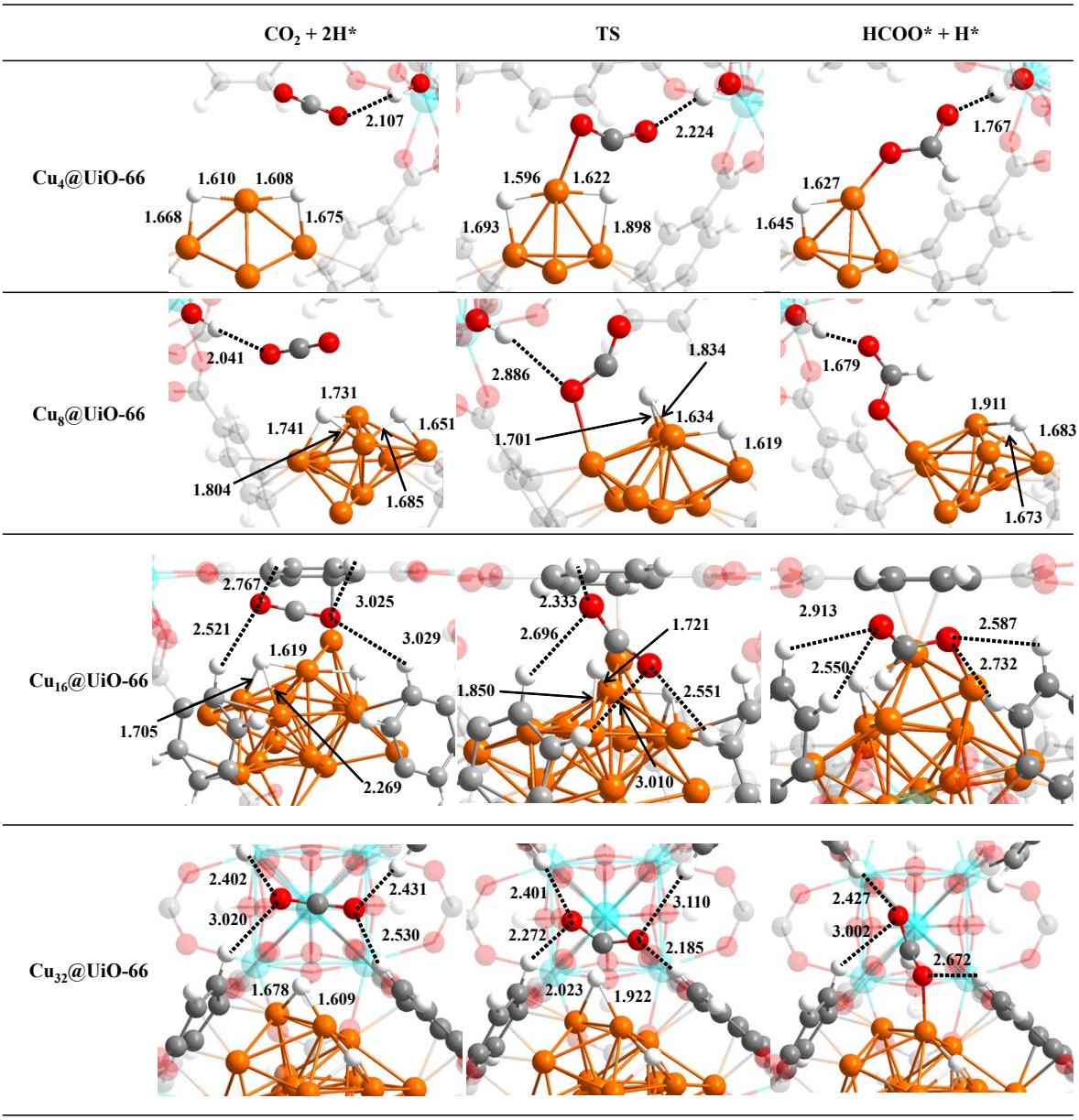

Figure S5. The optimized structures of CO_2 hydrogenation on UiO-66-confined Cu_n (n = 4, 8, 16, 32) with key bond distance (Å), where H, C, O, Zr and Cu are in white, grey, red, turquoise and orange, respectively.

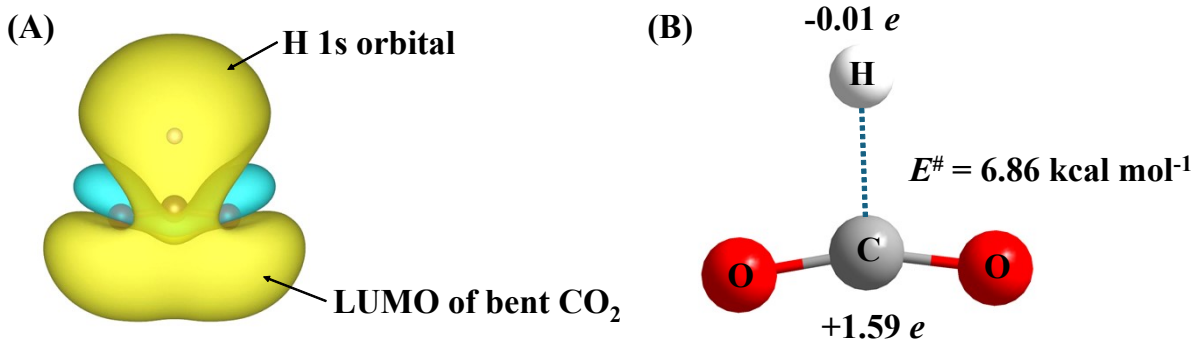

Figure S6. (A) Overlap between H 1s orbital and lowest unoccupied molecular orbital (LUMO) of bent CO_2; (B) Optimized structure of CO_2 hydrogenation to HCOO in gas phase, where charge state of C and H atoms are labeled, $E^{\#}$ is the activation barrier in kcal mol^{-1}

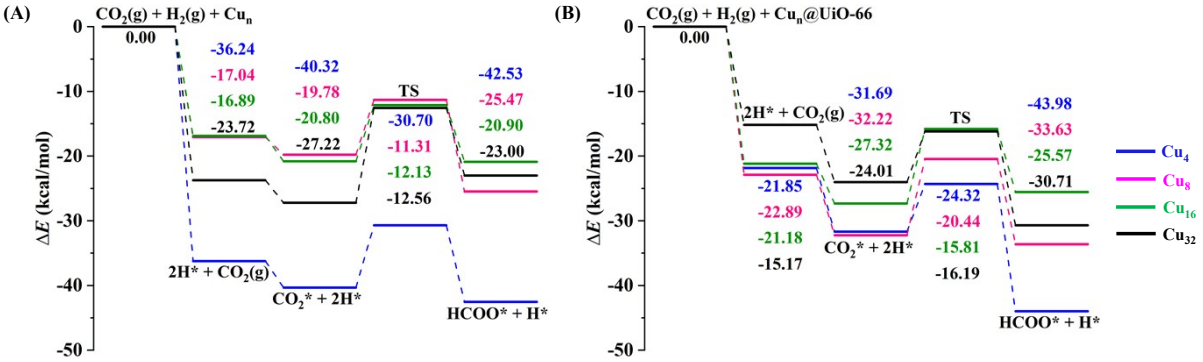

Figure S7. ΔE profiles for CO_2 hydrogenation to HCOO on (A) non-confined and (B) UiO-66-confined Cu clusters.

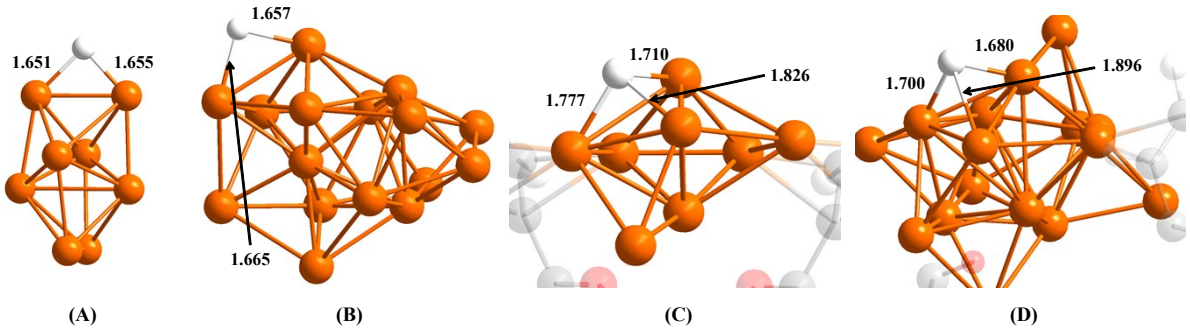

Figure S8. The optimized structures of H* on Cu_8, Cu_{16}, Cu_8@UiO-66 and Cu_{16}@UiO-66 with key bond distance (Å), where corresponding adsorption energy of H* (ΔE_H) is presented in **Table S1**.

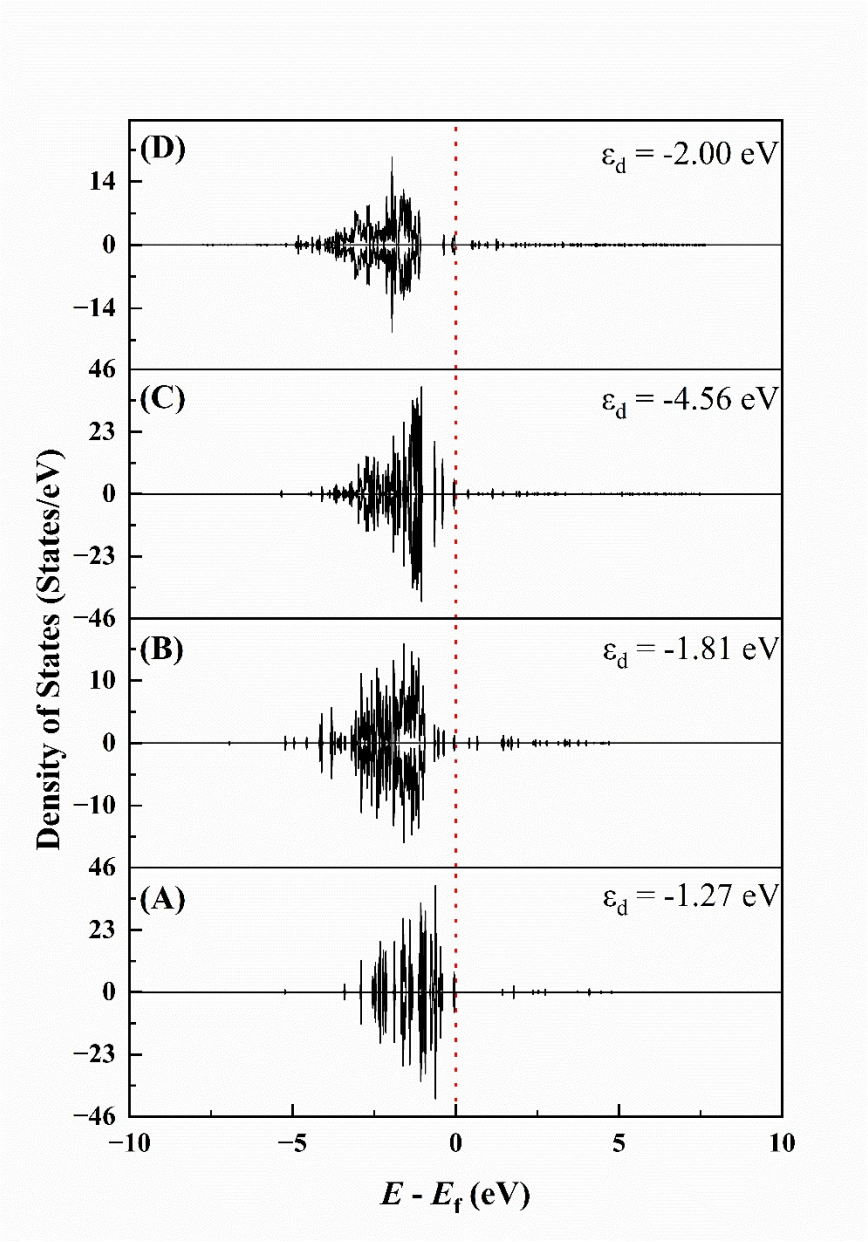

Figure S9. The local density of 3d states of adsorption sites for H* including corresponding d-band center (ε_d) on (A) Cu_8, (B) Cu_{16}, (C) Cu_8@UiO-66 and (D) Cu_{16}@UiO-66, respectively.

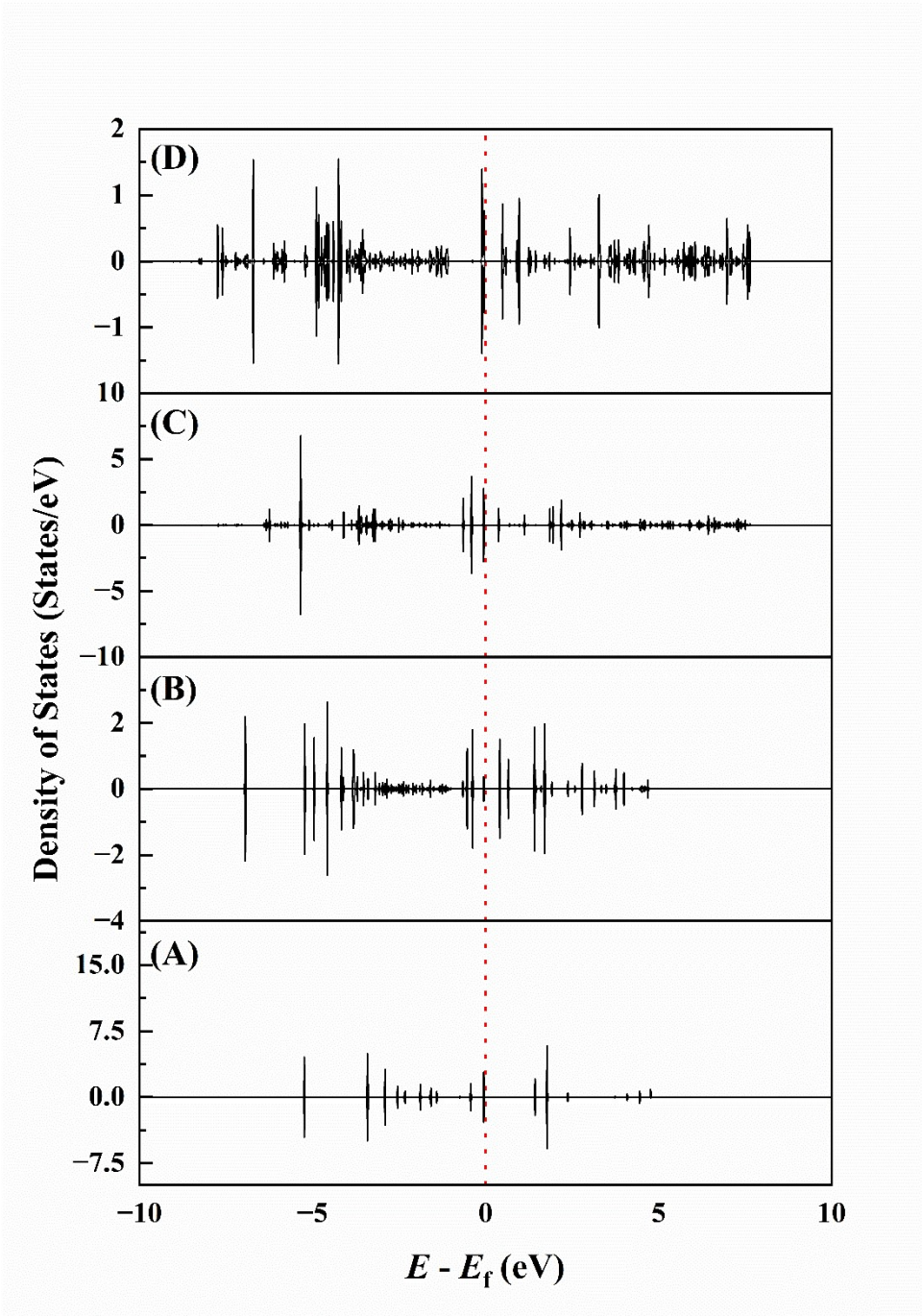

Figure S10. The local density of 4s states of adsorption sites for H* on (A) Cu_8, (B) Cu_{16}, (C) Cu_8@UiO-66 and (D) Cu_{16}@UiO-66, respectively.

S2. Selection of active sites

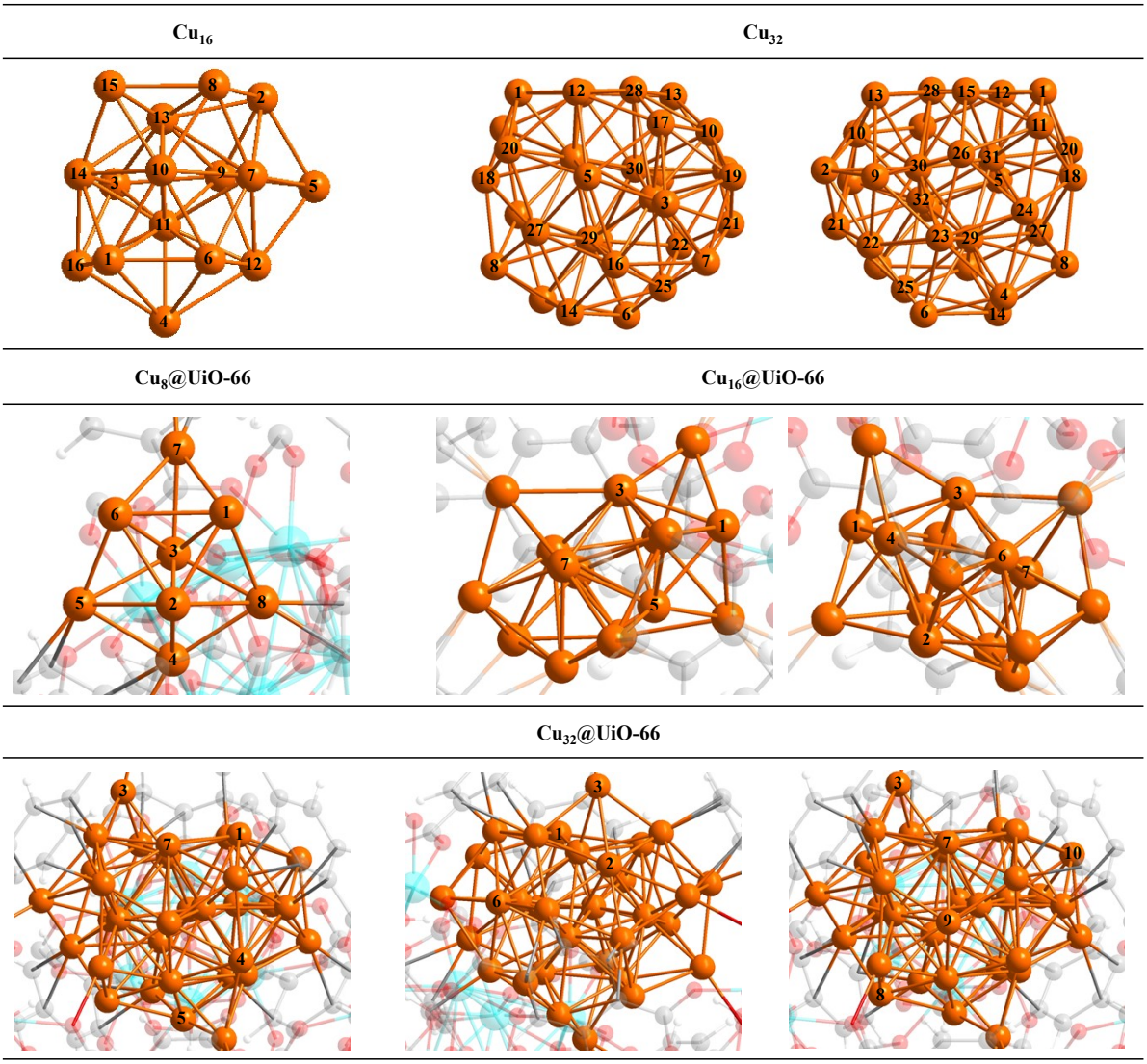

Figure S11. Graphical illustration of Cu sites (CS) assigned for H_2* on Cu_{16}, Cu_{32}, Cu_8@UiO-66, Cu_{16}@UiO-66 and Cu_{32}@UiO-66, respectively.

In order for an effective C-H interaction, selection of active site for CO_2 hydrogenation is limited to the location of dissociative chemisorption of H_2 reported in our previous study.[1] The initial state of which is H_2*. We therefore performed calculations of H_2* on available Cu site (CS) and accordingly computed its ΔE in determining which CS was chosen for H_2 dissociation. Cu_4 and Cu_8 were not examined since their optimal CSs on H_2 dissociation have already been reported by other studies.[2–5] The initial structure of H_2* on Cu_4 and Cu_8 were

therefore sourced from the literature. On Cu_{16}, all CSs have been assessed (**Figure S11**) and CS8 presents the greatest ΔE of H_2* in contrast to that of other CSs (**Table S2**). On Cu_{32}, CS1 – CS28 were examined as CS29 – CS32 are highly packed by surrounding CSs and located at the core of cluster, resulting in zero activity to H_2 adsorption. As demonstrated in **Table S2**, CS21 is the optimal site for reaction. For Cu_4@UiO-66, only one CS is available to H_2 adsorption as H_2* on the rest of three, which are bonded with UiO-66 as presented in **Figure 1e**, is preferably located at the nearby of window site of UiO-66. For Cu_8@UiO-66 (**Figure S11**), CS6 show the greatest ΔE of H_2* (**Table S2**). CS4 – CS5 and CS7 – CS8, which are in interfacial interactions with UiO-66, as well as CS3 that is highly coordinated by other CSs, show relatively lower adsorption energy in contrast to CS6 (**Table S2**). Therefore, CSs featured with similar characteristics were excluded in the calculations when we came to UiO-66-confined Cu_{16} and Cu_{32}, where seven and ten CSs were examined, respectively (**Figure S11**). According to **Table S2**, CS2 and CS10 are the results of selection of active site on Cu_{16}@UiO-66 and Cu_{32}@UiO-66.

Table S2. Adsorption energies (ΔEs) of H_2* on Cu sites (CS) of Cu_{16}, Cu_{32}, Cu_8@UiO-66, Cu_{16}@UiO-66 and Cu_{32}@UiO-66, where CS are Cu sites shown in **Figure S11**.

Catalyst / ΔE (kcal mol^{-1})	Cu_{16}	Cu_{32}	Cu_8@UiO-66	Cu_{16}@UiO-66	Cu_{32}@UiO-66
CS1	-4.64	-7.73	-3.05	-2.64	0.04
CS2	-5.99	-10.39	-5.01	-9.09	-0.34
CS3	-1.52	-7.66	-2.70	-5.83	-3.58
CS4	-3.50	-10.05	-3.04	-5.15	-3.69
CS5	-3.94	-7.14	-1.00	-0.97	-4.66
CS6	-4.71	-5.83	-6.63	-3.65	2.69
CS7	-3.95	-8.55	-2.53	-2.11	2.07
CS8	-11.65	-9.12	-1.13		-0.48
CS9	-7.55	-8.34			-3.77
CS10	-6.24	-6.23			-5.21
CS11	-3.56	-7.94			
CS12	-4.79	-9.04			
CS13	-2.16	-9.08			
CS14	-11.38	-6.39			

CS15	-8.39	-4.70
CS16	-2.12	-8.07
CS17		-4.31
CS18		-3.60
CS19		-4.82
CS20		-9.26
CS21		-11.62
CS22		-8.20
CS23		-6.21
CS24		-6.39
CS25		-9.78
CS26		-7.76
CS27		-10.77
CS28		-11.40

S3. Validations of input parameter

For Cu clusters, which are defined as non-periodic systems, are calculated based on 1 × 1 × 1 k-point scheme in precluding spurious interactions from periodic images, thus improving the accuracy on describing their localized electronic states.[6] By contrast, periodicity is confirmed on UiO-66 composites. Herein, this section aims to search for acceptable k-point grid on sampling their Brillouin zone. Cu_4@UiO-66 was calculated at 1 × 1 × 1, 2 × 2 × 2, 3 × 3 × 3, 4 × 4 × 4, 5 × 5 × 5, 6 × 6 × 6, 7 × 7 × 7, respectively. As demonstrated by **Figure S12**, less-than 0.1 kcal mol^{-1} derivation between electronic energies at 1 × 1 × 1 and 7 × 7 × 7 is presented, where ΔE_{diff} is the energy difference of various k-point grid using electronic energy computed at 1 × 1 × 1 as benchmark.

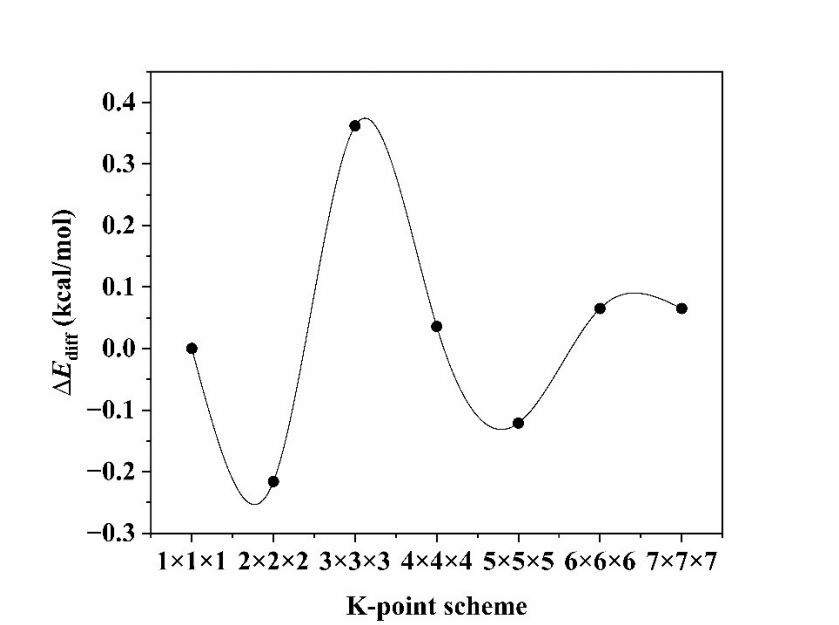

Figure S12. ΔE_{diff} based on 1 × 1 × 1 along various k-point scheme for Cu_4@UiO-66

S4. References

(1) Ye, Z.; Xie, W.; Chen, H.; Kawi, S. How UiO-66 Confinement Tunes Copper Catalytic Activity on H2 Dissociation? *Mol. Catal.* **2025**, *586*, 115451. https://doi.org/10.1016/j.mcat.2025.115451.

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