

Electronic Supporting Information (ESI)

Enhanced Catalytic Performance of a Single-Atom Cu on Mo₂C toward CO₂/CO Hydrogenation to Methanol: A First- Principles Study

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CO₂ hydrogenation to methanol (A)

H₂O formation from methanol desorption (A2)

Figure S1 showed water formation from the desorbed CH₃OH using 99 kJ mol⁻¹ from CO₂ hydrogenation (route A2). The oxygen adsorbed on the surface is hydrogenated through the heterolytic transition state (TS1), leading to the O-H bond, and the other H* proton adsorbed at the Cu/Mo₂CO_x interface. TS2, with an energy barrier of 100 kJ mol⁻¹, forms water. After its desorption using 65 kJ mol⁻¹, the initial Cu/Mo₂CO_x surface is recovered.

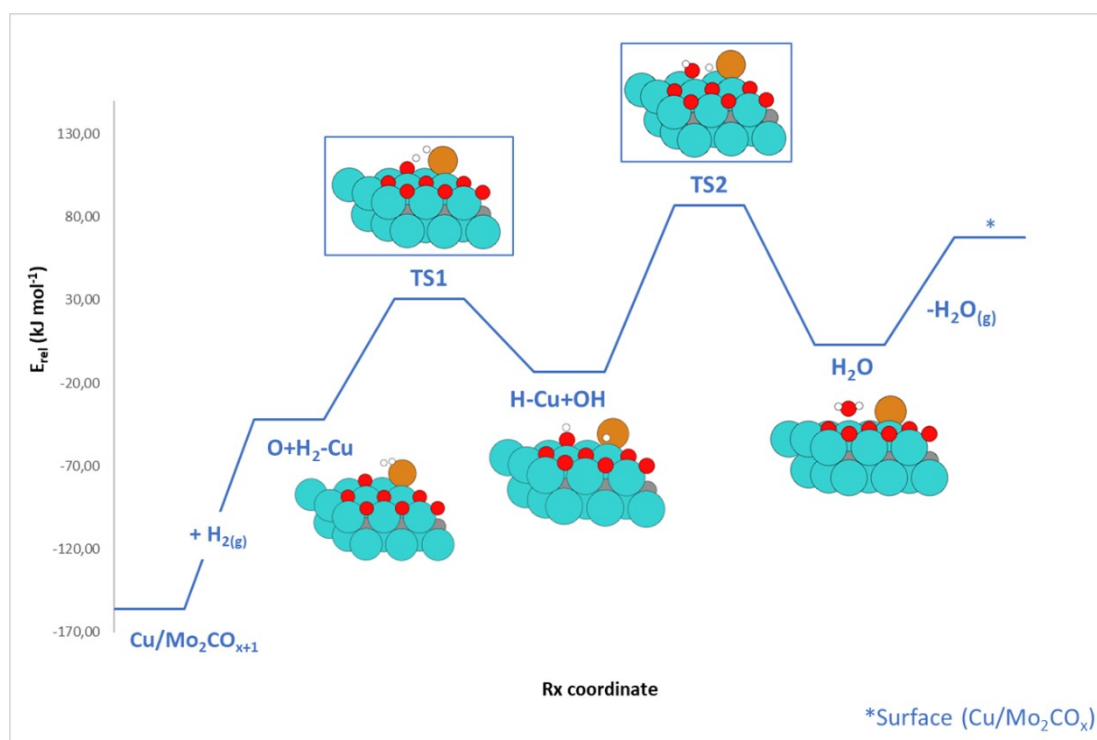


Figure S1. Energy profile for the reaction of O* and H₂ to form water from CH₃OH desorption. Energies of minimums and transition states (framed) are referenced against the sum of the initial reactants and catalyst energies in kJ mol⁻¹ (E_{rel}).

Methanol formation via the A3 pathway

The A3 pathway has been characterized by locating the related intermediates and transition states. However, it is less feasible than the former (A2) due to its higher energy barriers. Its profile is shown in Figure S2. Once HCOO* is obtained, in the same way as described above, a new H₂ molecule adsorbs to proceed with the hydrogenation. Conversely, the HCOOH* species is obtained through an energy barrier of 87 kJ mol⁻¹. This heterolytic transition state (A3-TS2) leads to the HCOOH* and the other two H* proton adsorbed at the Cu/Mo₂C interface. Afterward, one H* at the interface promotes the H₂COOH formation. This step requires overcoming an energy

barrier of 86 kJ mol^{-1} (**A3-TS3**). At this point, we describe the subsequent steps previously reported.²⁷ To get to methanol, the next step is cleaving the C-OH bond of H_2COOH^* to get H_2CO . At the same time, water is also obtained. The energy barrier is about $116.6 \text{ kJ mol}^{-1}$, which is the highest of the energy profile (**A3-TS4**). Once water is formed, it transfers hydrogen to formaldehyde, producing methoxy. This step is exoenergetic and has a small energy barrier (**A3-TS5**). The final step is a second proton transfer from the OH^* group to the methoxy to yield methanol species. This last transition state (**A3-TS6**) goes through an energy barrier of 56.8 kJ mol^{-1} . Finally, methanol desorbs with an energy cost of 86 kJ mol^{-1} .

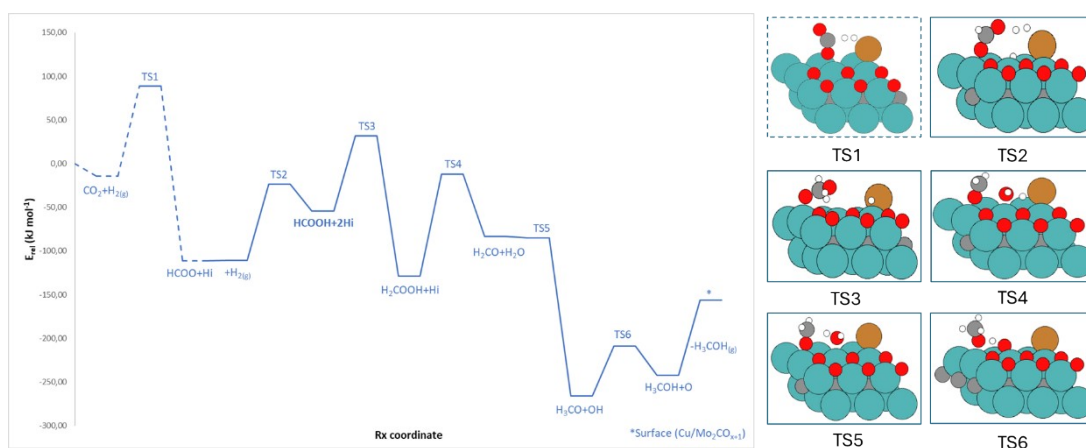


Figure S2. Energy profile (**A3**) for the reaction of CO_2 and 2H_2 to form methanol from HCOO^* species. Energies of minimums and transition states (framed) are referenced against the sum of the initial reactants and catalyst energies in kJ mol^{-1} (E_{rel}).

Gibbs profile of CO₂ hydrogenation (A2)

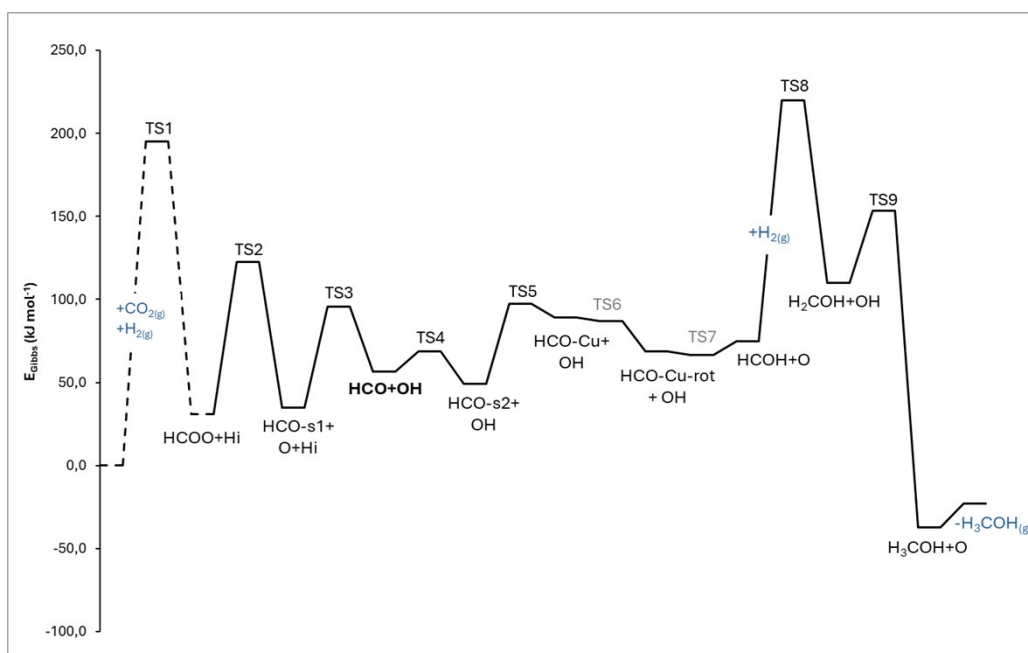


Figure S3. Energy profile by Gibbs energies for the reaction of CO₂ and 2H₂ to form methanol from HCOO* species (A2). Gas phase species are in blue and non-barrier TS in grey. Thermodynamic corrections were calculated using statistical thermodynamics at 503.15 K and pressure values of 5 bar (CO₂, H₂O), 15 bar (H₂) and 2.5 bar (CO, CH₃OH) to build the Gibbs energy profile.

CO hydrogenation to methanol (B): HCO routes

The corresponding HCO energy profiles, just considering the energetics of the reaction intermediates, are depicted in **Figure S4**. The most feasible route (B2) is described in the HCOH-path section's main text, while the rest of the pathways are explained below in this ESI section.

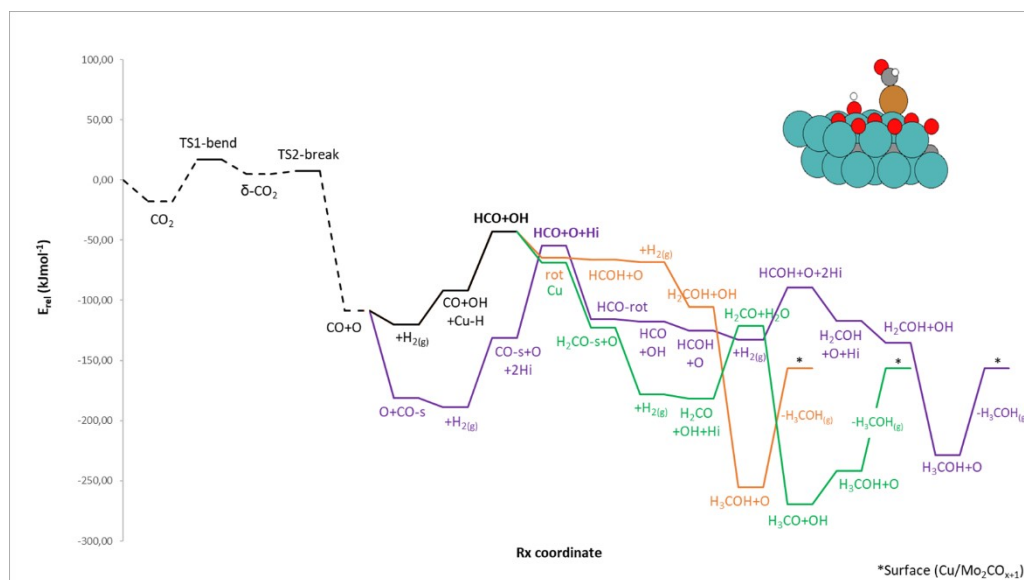


Figure S4. Energy profiles for the reaction of CO₂ and 2H₂ to form methanol through three different paths from HCO* species: HCOH* (orange traces), H₂CO* on support (green trace), and HCO on support (purple trace), respectively. Dashed and black traces are steps common for all profiles. Energies of minimums and transition states (framed) are referenced against the sum of the initial reactants and catalyst energies in kJ mol⁻¹ (E_{rel}).

HCOH-support path (B2sup)

Figure S5 considers the possibility of forming HCO species on the support (Mo₂CO_x) instead of on top of the Cu center. Here, we describe the energetics of the related transition states (**B2sup-TS**) and their energetic feasibility.

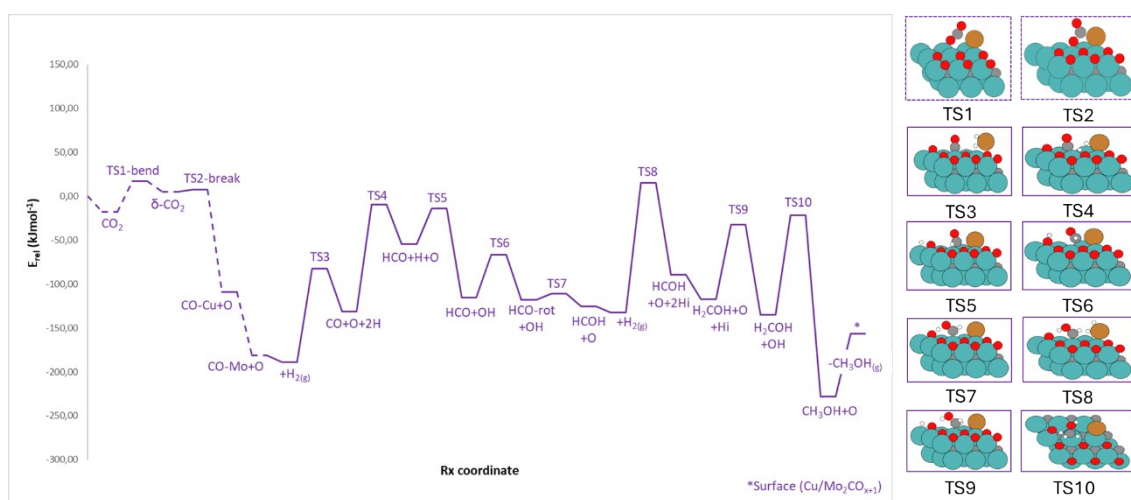


Figure S5. Energy profile for the reaction of CO₂ and 2H₂ to form methanol from HCO* species on the Mo₂Cox support. Dashed traces are steps common for all profiles. Energies of minimums and transition states (framed) are referenced against the sum of the initial reactants and catalyst energies in kJ mol⁻¹ (E_{rel}).

This mechanism starts with the CO* migration from Cu to the Mo₂C support, where its stabilization increases considerably, releasing 72 kJ mol⁻¹. In this case, the C atom of CO* is directly bonded to Mo hollow sites. After that, a new molecule of H₂ enters the system. In contrast to the previously evaluated paths, its activation proceeds via a homolytic transition state (**B2sup-TS3**), having 106 kJ mol⁻¹ as an energy barrier, and forms a couple of H-Cu bonds. This is probably due to the distance between the CO* group and the Cu interface, which does not allow heterolytic cleavage. Once this activation occurs, the mechanism proceeds to the formation of HCO* species by transferring the hydride from the Cu/Mo₂CO_x interface to the CO* group at 122 kJ mol⁻¹ (**B2sup-TS4**). Afterward, we considered the OH* formation by hydrogen transfer of the second H* from H₂, facilitating the next reaction step. Forming OH* requires 40 kJ mol⁻¹ as an energy barrier (**B2sup-TS5**). Next, an extra step enables the hydrogenation process. HCO* rotates until the oxygen atom remains oriented toward the OH* group via an energy barrier of 49 kJ mol⁻¹

(**B2sup-TS6**). After that, the proton transfer from OH* to HCO* over Mo sites leading to O* and HCOH* respectively required only 7 kJ mol⁻¹ (**B2sup-TS7**). This last species adsorbed on the support is more stable than the previous HCOH* species adsorbed on Cu obtained via the COH* and HCOH* routes. Once the HCOH* species is obtained, a second H₂ molecule is introduced into the system to proceed with the hydrogenation reaction. This H₂ activation, the most energy-demanding of this energy profile, proceeds via a homolytic cleavage (**B2sup-TS8**) due to the distance between the HCOH* and Cu interface. This step forms two new H-Cu bonds, having an energy barrier equal to 148 kJ mol⁻¹, and turns out to be the most energy-demanding one from this profile. This transition state increases its energy barrier by 42 kJ mol⁻¹ compared to the first homolytic activation of H₂ in this profile (**B2sup-TS3**). This increase could be caused by repulsion effects between the different compounds adsorbed in the system. However, one of these new H-Cu bonds enables the rapid formation of the H₂COH* species from one H* adsorbed from the Cu center to the carbon atom of the HCOH* species. Since this step has a negligible energy barrier, it is not included in the energy profile. The formation of the last C-H bond to form methanol does not occur by direct H* transfer to H₂COH*. Instead, H* is transferred from OH*, and the latter species shuttles the hydrogen to H₂COH*, leading to O* and CH₃OH*, respectively. The hydrogen transfer to adsorbed O* to form OH* has an energy barrier equal to 85 kJ mol⁻¹ (**B2sup-TS9**). The hydrogen transfer from OH* to H₂COH* produces methanol with an affordable energy barrier of 114 kJ mol⁻¹ (**B2sup-TS10**). Finally, methanol desorbs with an energetic cost of 72 kJ mol⁻¹.

Gibbs profile of CO₂ hydrogenation (**B2**)

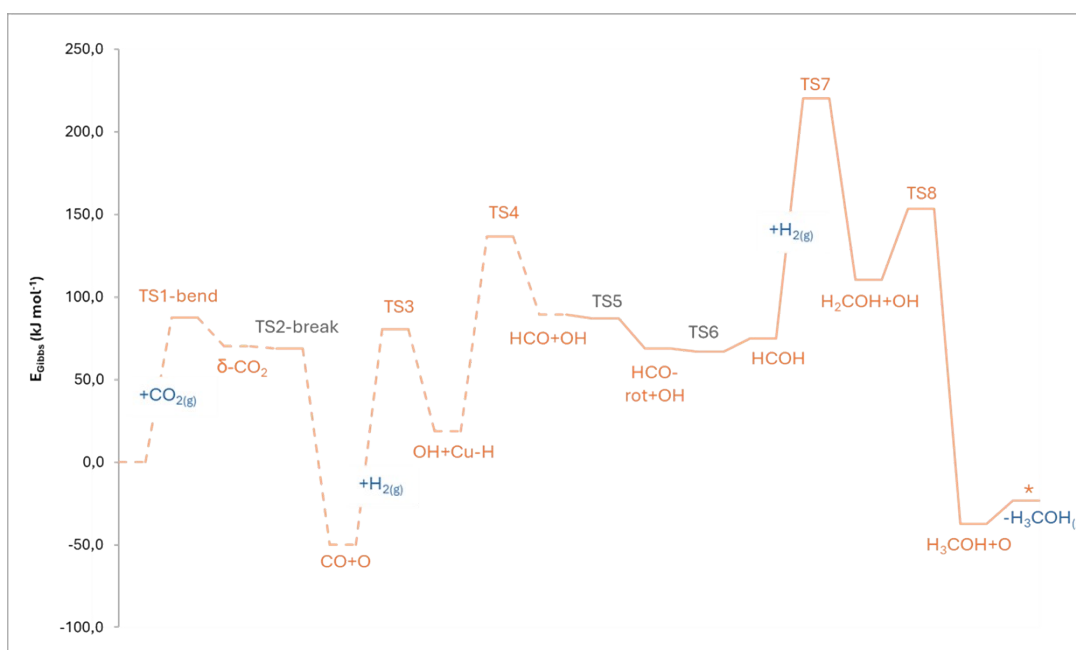


Figure S6. Energy profile by Gibbs energies of CO₂ and 2H₂ to form methanol from the HCOH* species (**B2**). Gas phase species are in blue and non-barrier TS in grey. Thermodynamic corrections were calculated using statistical

thermodynamics at 503.15 K and pressure values of 5 bar (CO_2 , H_2O), 15 bar (H_2) and 2.5 bar (CO , CH_3OH) to build the Gibbs energy profile.

Gibbs profile of CO_2 hydrogenation (**B2+B2sup**)

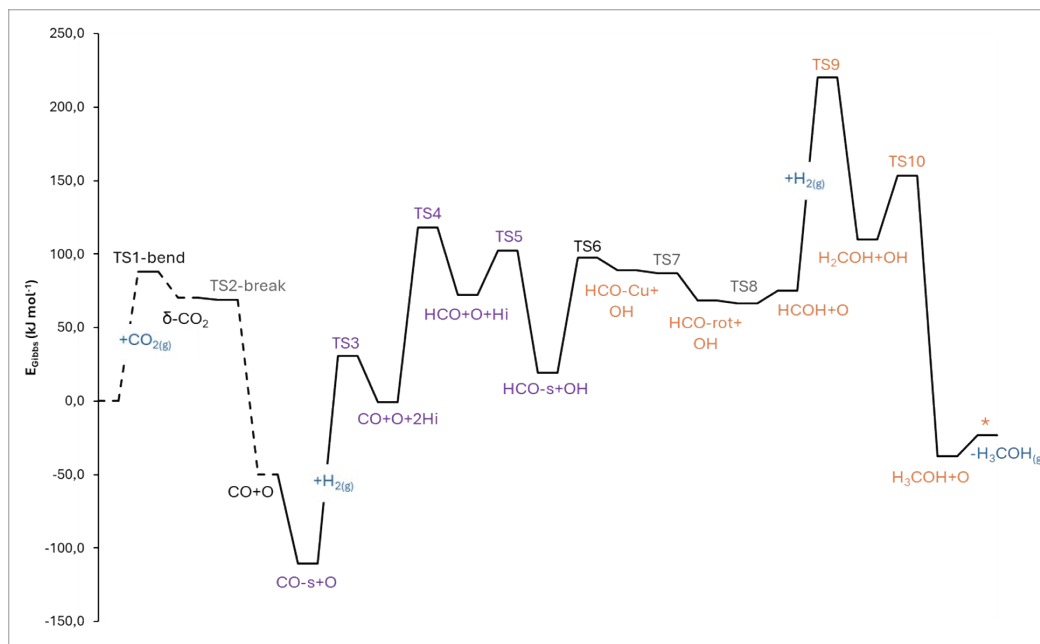


Figure S7. Energy profile by Gibbs energies of CO_2 and 2H_2 to form methanol from HCOH^* species on support (purple labels, **B2sup**) to HCOH^* species on Cu center (orange labels, **B2**). Gas phase species are in blue and non-barrier TS in grey. Thermodynamic corrections were calculated using statistical thermodynamics at 503.15 K and pressure values of 5 bar (CO_2 , H_2O), 15 bar (H_2) and 2.5 bar (CO , CH_3OH) to build the Gibbs energy profile.

H_2CO path (**B3**)

The last route, via the H_2CO^* species (**Fig. S8**), increases the number of more stable intermediates. The chemistry is evaluated on the Cu atom as a starting point ($\text{Cu-H}_2\text{CO}$) before moving to the Mo_2CO_x surface due to better stabilization ($\text{H}_2\text{CO-S}$). Thus, we subsequently study the possible transition states (**B3-TS**) shown by the profile and the energy barriers that confirm their potential feasibility. From the obtained HCO^* and OH^* species, the mechanism can proceed by a proton transfer from OH^* to the $\text{Cu}/2\text{D-Mo}_2\text{CO}_x$ interface to facilitate H_2CO^* and O^* formation (**B3-TS5**). This step has an energy barrier of 69 kJ mol^{-1} , raising the H_2CO^* intermediate bonded to the Cu atom. H_2CO^* is further stabilized upon migrating to the support, *i.e.*, Mo sites on Mo_2C , in a process that releases 53.7 kJ mol^{-1} . The second molecule of H_2 is needed to proceed further with the hydrogenation. H_2 adsorption releases 55.5 kJ mol^{-1} . The H_2 molecule then splits into two new bonds by one H atom on the co-adsorbed O^* , forming an OH^* group, and the other H atom adsorbs on the $\text{Cu}/2\text{D-Mo}_2\text{CO}_x$ interface via a heterolytic transition state (**B3-TS6**) of about 41.6 kJ mol^{-1} . This was followed by proton transfer from the interface H^* atom to the OH^* group to

give H_2O^* , which required $106.2 \text{ kJ mol}^{-1}$ (**B3-TS7**) as an energy barrier. This step is the second most energy-demanding step along this mechanism. At this point, two proton transfers are needed to obtain methanol. Water participates first by transferring a proton, forming methoxy (OCH_3^*) and an OH^* group. This OH^* then transfers a proton to methoxy, producing methanol. Both proton transfers have affordable energy barriers, *i.e.*, 60 and 61 kJ mol^{-1} (**B3-TS8**, **B3-TS9**). These last four steps and the respective transition states agree with the results obtained in our previous work on the hydrogenation of CO_2 .²⁷ Finally, methanol is desorbed, with an energy cost of 85 kJ mol^{-1} .

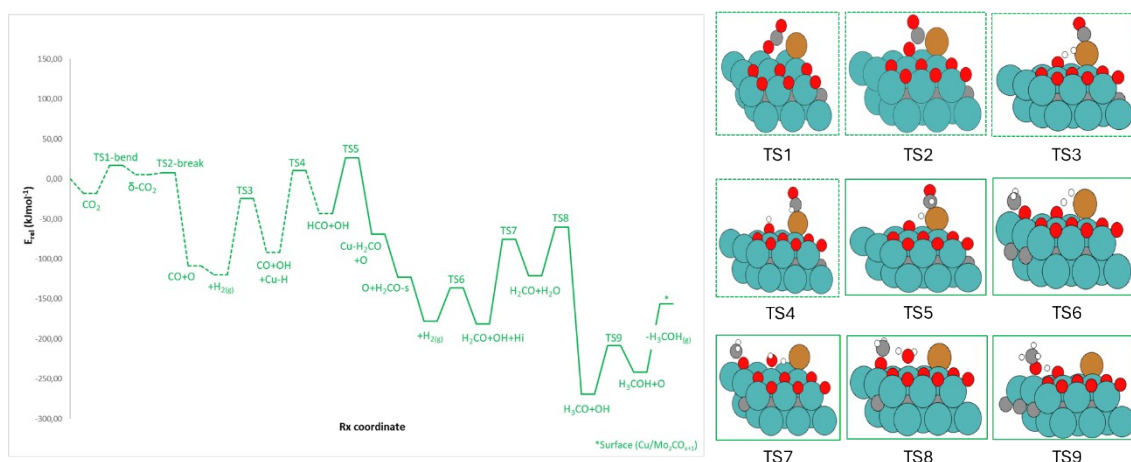


Figure S8. Energy profile for the reaction of CO_2 and 2H_2 to form methanol from H_2CO^* species. Red traces are steps common for all profiles. Energies of minimums and transition states (framed) are referenced against the sum of the initial reactants and catalyst energies in kJ mol^{-1} (E_{rel}).

RWGS pathways (C)

Description of Reverse Water–Gas Shift Reaction Mechanisms

The general pathways of RWGS following the formation of COOH^* (green traces) are described in **Figure S9**. There are two different pathways from this first intermediate. The soft green line shows the possible route on the $\text{Cu}/2\text{D-Mo}_2\text{C}$ 0.67 O ML interface from the CO-OH bond cleavage of the COOH^* species. After that, the CO desorbs, and the OH^* group remains on the surface. The latter group can be hydrogenated to water by the H^* atom adsorbed at the 0.67 O ML $\text{Cu}/2\text{D-Mo}_2\text{C}$ interface produced from the previous H_2 splitting to obtain COOH^* (**C2**). The dark green line shows the second possible path and considers the H^* to be the carbon atom of the COOH^* to produce formic acid (HCOOH^*) on the support. Then, the cleavage of one of the C-O bonds leads to HCO^* and OH^* groups adsorbed on the Mo sites of Mo_2C . The final step for water

formation is transferring a proton of the HCO* species to the OH* group. This last step also allows obtaining CO* species that can desorb to form CO_(g).

Next, we describe the mechanisms involving the (C3) HCOO* intermediate (black dashed line) in **Figure S9**. This intermediate is obtained at the Cu/2D-Mo₂C 0.67 O ML interface (A2-TS1), but the following reactivity is performed on the support (black and gray traces). In addition, the black path is divided into two mechanistic routes due to the difference in geometry and energy barriers by intermediates and transition states described below. The gray pathway shows that HCOO* splits into the O* atom at the Mo-hollow site and the HCO* intermediate, while the other H* atom remains at the metal-surface interface. The next step is to transfer a proton to O* to obtain the OH* group. In this case, HCO* is coordinated with the metal center. Then, the C-H bond cleavage simultaneously enables migration of the CO* over the Cu center and transferring H* to the O* instead of the H* adsorbed the Cu/2D-Mo₂C 0.67 O ML interface. So, the compound CO* is adsorbed on the top of the copper atom while the OH* group remains on the Mo-site surface and the H* atom at the interface. CO* can be desorbed, and the final step for water formation is the transfer of the interface proton to the OH* group. The black pathway shows that HCOO* is divided into HCO* and O* groups and an H* atom at the interface. In this case, the HCO* intermediate binds to the copper atom and is adsorbed to Mo-hollow. Due to the last geometry and position of the atoms described, this intermediate is more stable than its counterpart in the gray path. At this point, this route could take two different pathways (black and red traces). The black line continues with obtaining the OH* group. The intermediate HCO* transfers the proton to the next O* atom. Thus, CO* and OH* compounds are adsorbed on the Mo-hollows. The CO* can then be desorbed, and the final step, as on the dark-blue pathway, for water formation, is the transfer of a proton from the H* interface to OH*. Finally, the red line goes to the formation of OH* by O*-Mo and the atom H* at the interface. While OH* is obtained, HCO* remains attached to the copper atom and is adsorbed on Mo-hollow. The final step is performed by OH* and HCO* species, where HCO* transfers its proton to obtain H₂O* and CO*. This last step is shared with the COOH* route (dark-green route).

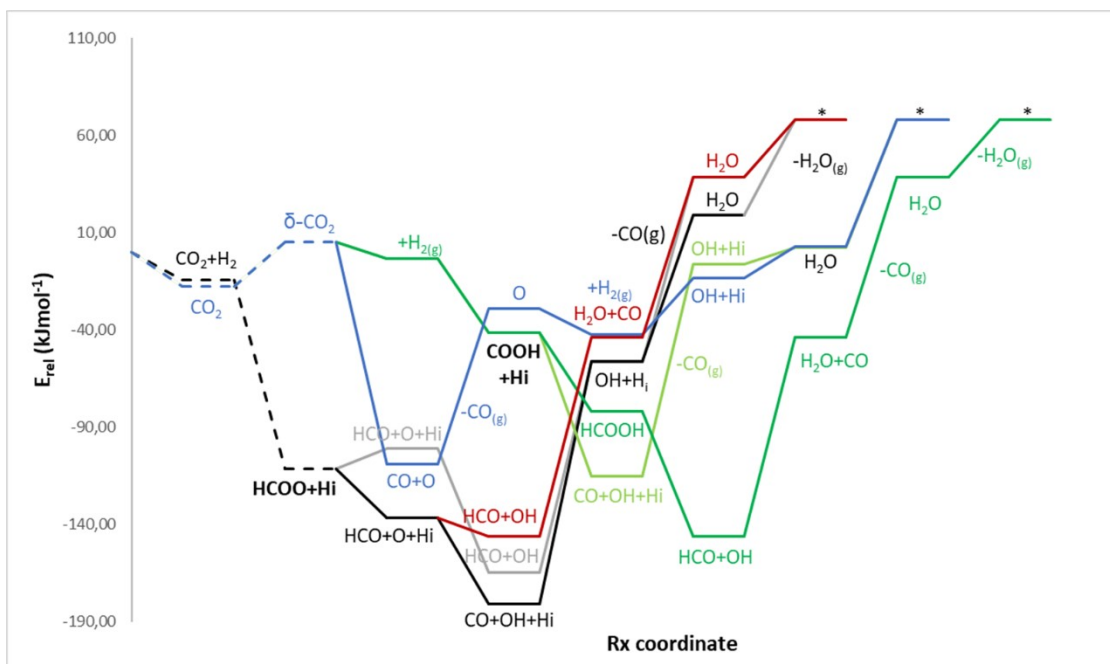


Figure S9. Energy profiles for the RWGS reaction of CO and H₂ to form water through three different pathways: CO*+O* (blue line), COOH* (green lines), or HCOO* (gray, red, and black lines), respectively. Intermediates in black are common in more than evaluated pathways. Energies are referenced against the initial reactants' energy in kJ mol⁻¹ (E_{rel}). The energy profile only depicts reaction intermediates and not transition states.

COOH path (C2)

Here, the most feasible route from COOH species (**Fig. S10**) to get water is presented. From the δ -CO₂ species, H₂ is physisorbed, releasing 9 kJ mol⁻¹. Next, the hydrogenation step to produce COOH* required an energy barrier of 128 kJ mol⁻¹ via a heterolytic transition state (**C2-TS1**) produces, considering formal oxidation states, a metal hydride, and a proton bonded to the oxygen from bent CO₂*. Then, CO* and OH* are produced by cleaving COOH*; CO* binds to the Cu atom while OH* is on a vacant Mo site. This step has a high energy barrier of 139 kJ mol⁻¹ (**C2-TS2**). This TS to obtain CO* is that route's rate-determining step (RDS). CO* desorption requires about 109 kJ mol⁻¹. The last step is obtaining water from the OH* bonded to Mo₂C, which is the proton transfer from the H* atom to the Cu/2D-Mo₂C 0.67 O ML interface in the OH* group. This last energy barrier is equal to 94 kJ mol⁻¹ (**C2-TS3**). Finally, water desorbs with an energy penalty of 65 kJ mol⁻¹.

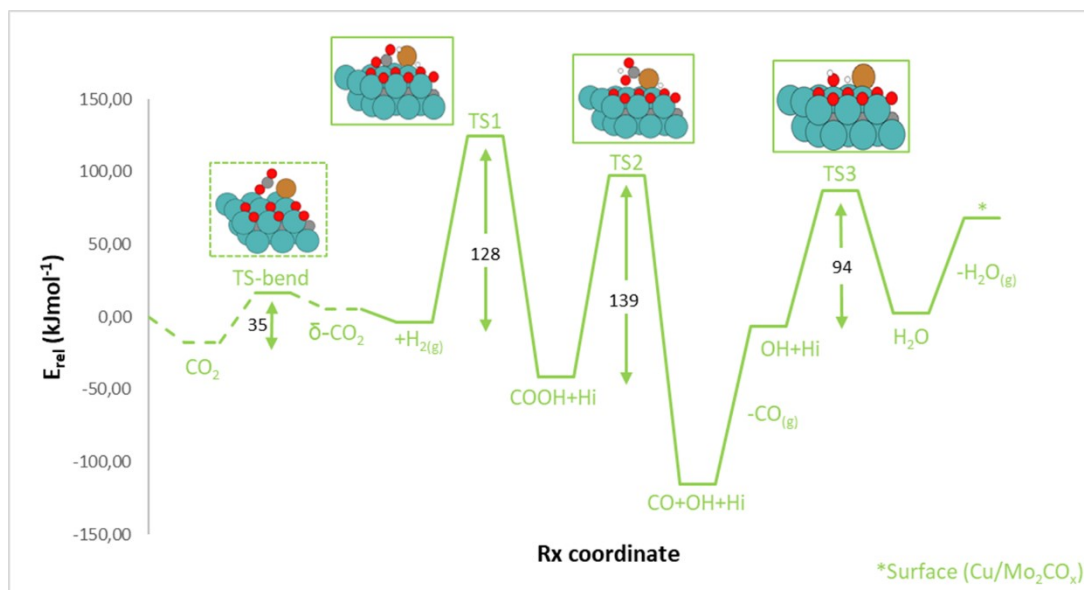


Figure S10. Energy profile for the reaction of CO_2 and H_2 to form water through COOH^* intermediate. Energies are referenced against the initial reactants' energy in kJ mol^{-1} (E_{rel}). Described TS are presented with their respective energies' barriers in the arrows.

HCOO paths (C3)

RWGS's main section mentions that water can also be formed from formate (HCOO^*). This route starts with the direct hydrogenation of CO_2 to obtain HCOO^* on the support (A2). Then, different pathways are described in the main text due to the present most feasible energy barriers: C31-gray (Fig. S11) and C32-black (Fig. S12).

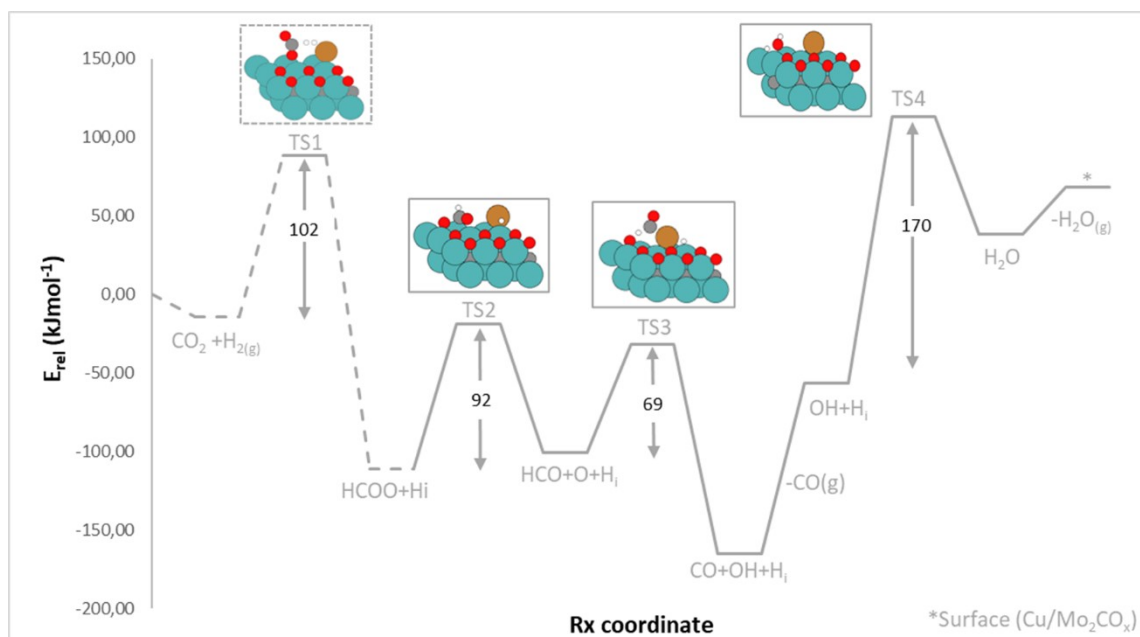


Figure S11. Energy profile for the reaction of CO₂ and H₂ to form water through HCOO* intermediate. Energies are referenced against the initial reactants' energy in kJ mol⁻¹ (E_{rel}). Described TS are presented with their respective energies' barriers, shown within the arrows.

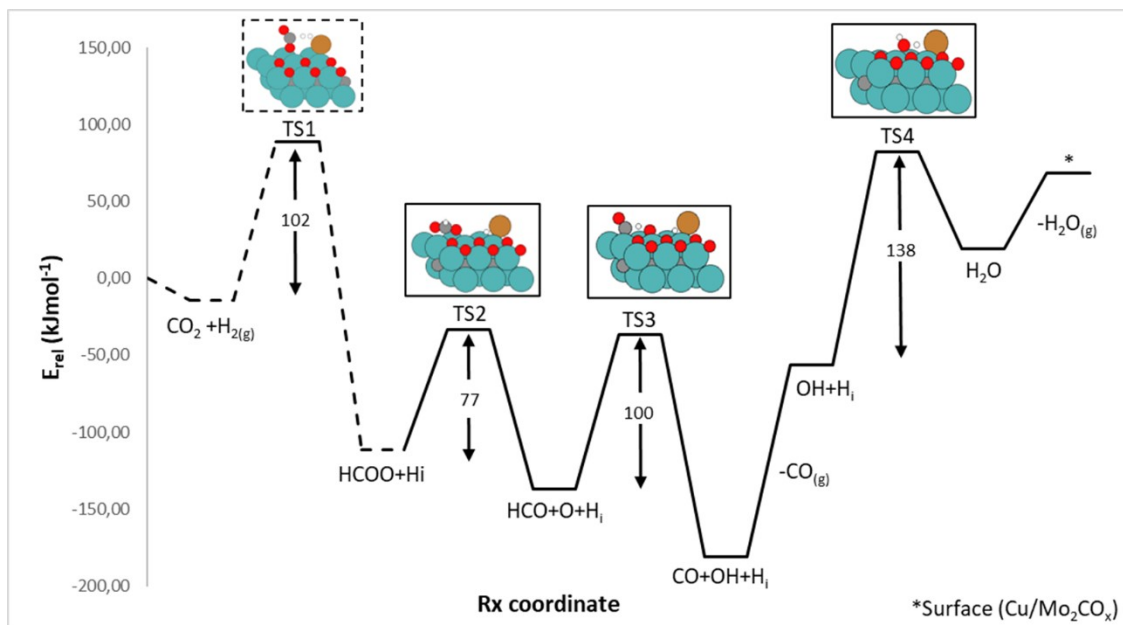


Figure S12. Energy profile for the reaction of CO₂ and H₂ to form water through HCOO* intermediate. Energies are referenced against the initial reactants' energy in kJ mol⁻¹ (E_{rel}). Described TS are presented with their respective energies' barriers, shown within the arrows.

Bader Charge Analysis

The calculated Bader values referred to in the main text are summarized in Tables S13-S15.

Table S13. Bader charge values corresponding to transition states of the hydrogen heterolytic cleavage for catalytic steps within the (a) CO₂ hydrogenation, (b) CO hydrogenation, and (c) RWGS reaction.

(a) Heterolytic cleavage H ₂		CO ₂ +H ₂		TS1		HCOO	
Atoms	Valence e ⁻	Bader	δ	Bader	δ	Bader	δ
H1	1	1,009	-	0,888	+	0,876	+
H2--Cu	1	0,987	+	1,118	-	1,312	-
C	2	1,849	+	2,310	-	2,426	-
Cu	11	10,935	+	10,886	+	10,544	+

(b) Heterolytic cleavage H ₂		CO+H ₂		TS3		OH+Cu-H	
Atoms	Valence e ⁻	Bader	δ	Bader	δ	Bader	δ
H1--O	1	0,993	+	0,511	+	0,415	+
H2--Cu	1	1,014	-	1,309	-	1,246	-
Cu	11	10,779	+	10,734	+	10,663	+
O	7	6,917	+	7,044	-	7,122	-

(c) Heterolytic cleavage H ₂		H ₂ [*]		TS		OH [*] + H [*]	
Atoms	Valence e ⁻	Bader	δ	Bader	δ	Bader	δ
O7-H1	1	0,935	+	0,520	+	0,411	+
Cu-H2	1	1,027	-	1,340	-	1,234	-
O7	7	6,912	+	7,038	-	7,118	-
Cu	11	10,860	+	10,805	+	10,753	+

Table S14. Bader values on the analysis of the transition states along the CO₂ activation pathway.

CO ₂ activation		CO ₂		TS1 (157°)		CO ₂ -bend (136°)		TS2		CO ₂ -break	
Atoms	Valence e ⁻	Bader	δ	Bader	δ	Bader	δ	Bader	δ	Bader	δ
O1	7	7,075	-	7,097	-	7,093	-	6,973	+	7,062	-
O2	7	7,111	-	7,053	-	7,029	-	7,070	-	6,909	+
O1-C-O2	2	1,837	+	2,040	-	2,405	-	2,768	-	2,963	-
Cu-O2	11	10,891	+	10,897	+	10,783	+	10,765	+	10,766	+

Table S15. Bader charge values corresponding to transition states of the hydrogen homolytic and heterolytic cleavage.

H ₂ activation		H ₂		TS		2H [*]	
Atoms	Valence e ⁻	Bader	δ	Bader	δ	Bader	δ
H1	1	1,002	-	1,060	-	1,223	-
H2	1	1,001	-	1,185	-	1,231	-
H1-C	1	0,945	+	0,921	+	0,949	+
H2-C	1	0,941	+	0,912	+	0,923	+
C	2	3,059	-	3,091	-	3,050	-
Cu	11	10,905	+	10,581	+	10,656	+