

Atom-by-atom design of Cu/ZrO_x clusters on MgO for CO₂ hydrogenation using liquid-phase atomic layer deposition

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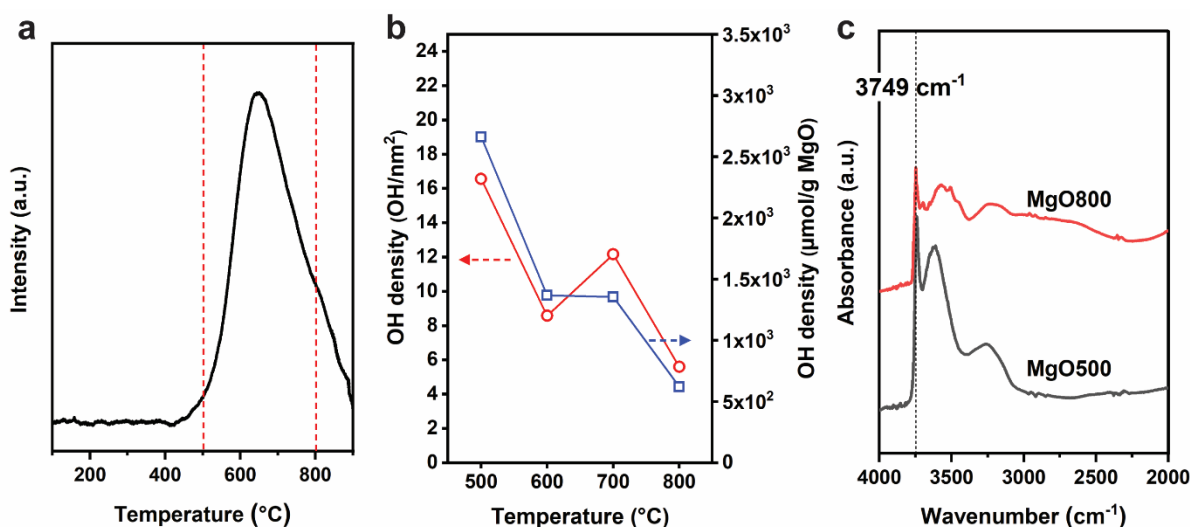
Supplementary Method

Supplementary Method 1. Catalysts preparation

After depositing the target metals on the support, the solution containing this substrate was centrifuged three times after redispersing the substrate in ethanol between washes. The collected powder was initially dried in the fume hood and further dried in the oven at 120 °C overnight. The dried powder was calcined in the furnace by ramping the temperature to 350 °C with a rate of 1 °C/min.

As impregnation controls, catalysts with the same metal components were prepared via incipient wetness impregnation (IWI) and were denoted by adding (I) in the name of catalysts. The pore volume of the corresponding supports was first measured via N₂ adsorption/desorption analysis (3Flex, Micromeritics). The precursor solution was prepared by dissolving copper (II) nitrate hydrate (Sigma-Aldrich, 99.999%), zirconium (IV) oxynitrate hydrate (Sigma-Aldrich, 99%), or zinc nitrate hexahydrate (Sigma-Aldrich, reagent grade, 98%) in deionized water where the volume was equivalent to the pore volume of the target support. The prepared solution was then mixed with the support and the mixture was first dried at 50 °C and then further dried at 120 °C overnight. To match the catalysts prepared by the liquid-phase ALD, the quantity of Cu and Zn impregnated on MgOZrO₂ was determined based on the quantity of deposited Zr in the fifth layer. For Cu(I)/ZrO₂, the same amount of Cu was impregnated as in Cu/ZrO₂. As benchmark catalysts, a commercial Cu/ZnO/Al₂O₃ optimized for water-gas shift reaction (denoted as HiFUEL W220, the composition is reported in [Supplementary Table 1](#)) and an industrial methanol synthesis Cu/ZnO/Al₂O₃ catalyst (63.3 wt.% CuO, 25 wt.% ZnO, 10 wt.% Al₂O₃, and 1.5 wt.% MgO fume, denoted as a commercial Cu/ZnO/Al₂O₃) were purchased from Alfa Aesar and ground into a powder. All the resulting catalysts were sieved (mesh size 100; 150 μm) before the catalytic activity test.

Supplementary Figures

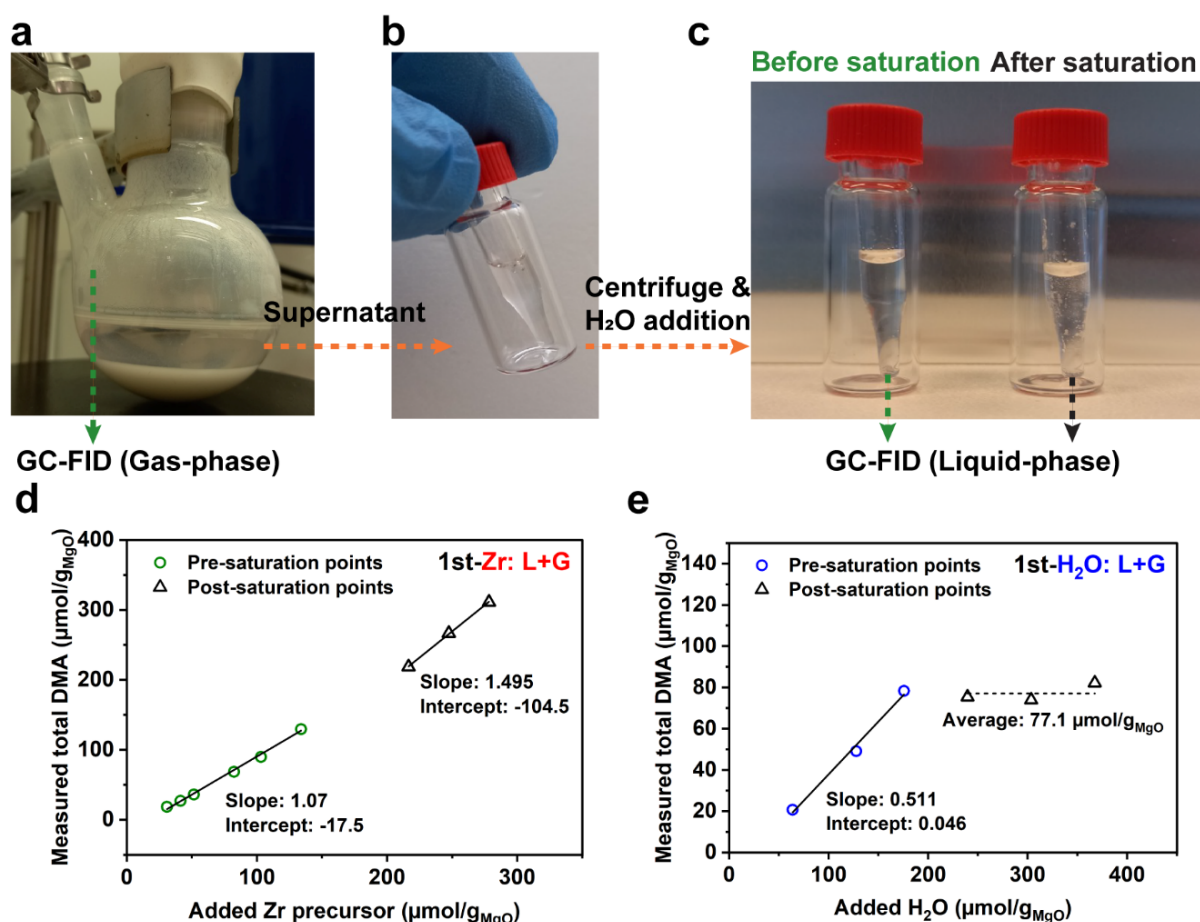


Supplementary Figure 1. (a) TPD profile of MgO500 under He flow after in situ thermal treatment at 500 °C under He flow for 1 h to remove any adsorbed gases that might have resulted from transferring the MgO into the U-shaped quartz reactor. (b) Hydroxyl densities of MgOs treated at different temperatures in two different units. (c) DRIFT spectra of as-synthesized MgOs treated at different temperatures.

Supplementary Notes

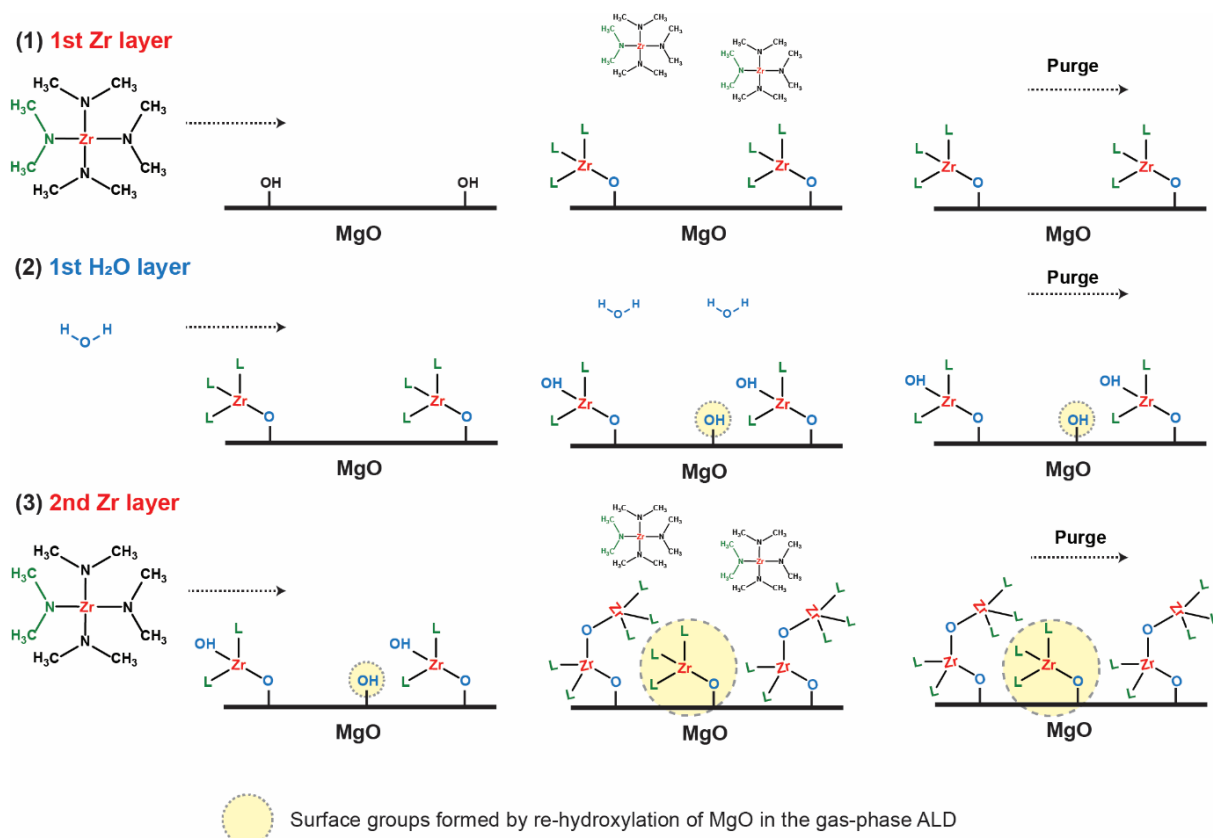
Supplementary Note 1. MgO500 calcined at 500 °C exhibited abundant defects and the basicity could be varied depending on the coordination number.¹ Increasing the thermal treatment temperature to 800 °C led to a decrease in the OH density in both units per surface area or per gram of MgO due to both dehydroxylation and sintering of MgO. As-synthesized MgO500 had a broad peak above 600 °C in the TPD profile resulting from desorption of thermally stable OH groups in MgO500 even after the thermal treatment at 500 °C. (Supplementary Fig. 1a). The hydroxyl density of MgO500 (16.6 OH/nm²) was considerably higher than the hydroxylated silica used in our previous work (8 OH/nm²)², due to defect sites being stabilized by the formation of hydroxyl groups (Supplementary Fig. 1b).

In the diffuse reflectance infrared Fourier transform (DRIFT) spectra, the peak at 3749 cm⁻¹ observed in the MgO500 still remained after the thermal treatment at 800 °C and was attributed to OH groups at a corner site of MgO³ (Supplementary Fig. 1c), where the lower coordinated Mg and O (Mg_{LC} and O_{LC}, respectively) were reported to have higher Lewis acidity and basicity than the higher coordinated species⁴.

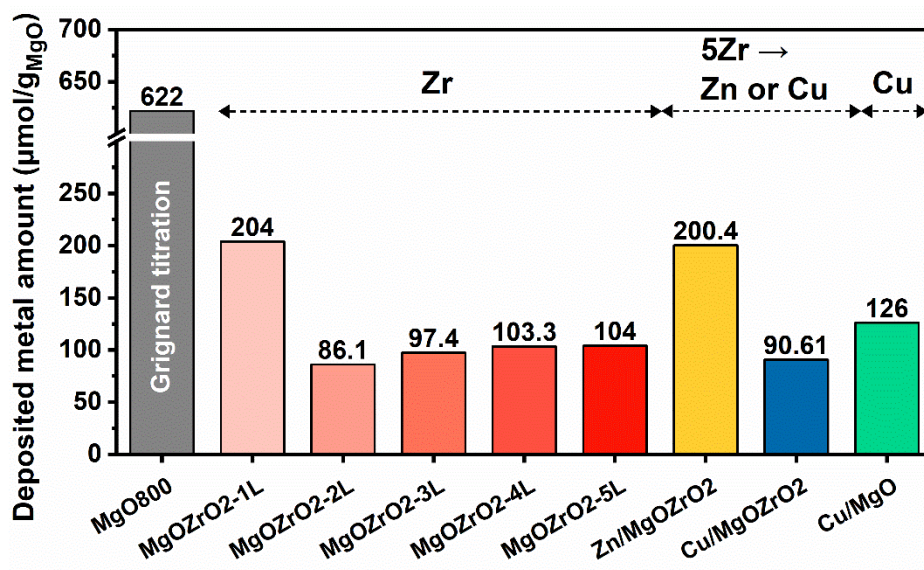


Supplementary Figure 2. Photos of (a) a round bottom flask after settling the powder, (b) the resulting extracted supernatant solution, and (c) the supernatant solution after centrifugation and the following addition of a minute amount of water with the resulting precipitates in the right-hand side GC vial. (d) Zr precursor and (e) H₂O titration lines obtained from both the gas- and liquid-phases. Please see the Methods section for details about ZrO_x cluster deposition.

Supplementary Note 2: The surface of MgO800 was initially titrated with the Zr precursor (Fig. 2a). After 60 min of reaction time, the amount of produced dimethylamine (DMA) was quantified (Fig. 2b). By repeating these steps, we were able to measure the point at which Zr saturates the bare MgO800 surface (Fig. 2c). Before this saturation, the amount of produced DMA increased linearly as a ligand was released when the surface hydroxyl was consumed. Once all accessible hydroxyls were consumed by the reaction with the Zr precursor, no more DMA was produced despite continued precursor injections. The intercept between these two regimes corresponds to the stoichiometric quantity of Zr precursor needed to saturate the surface of MgO800. As a counter reactant, H₂O was injected into the solution containing MgO800 saturated with the first Zr layer. Using an identical way as the Zr precursor titration, we obtained the H₂O titration curve and the saturation point for the first H₂O titration (Fig. 2d).

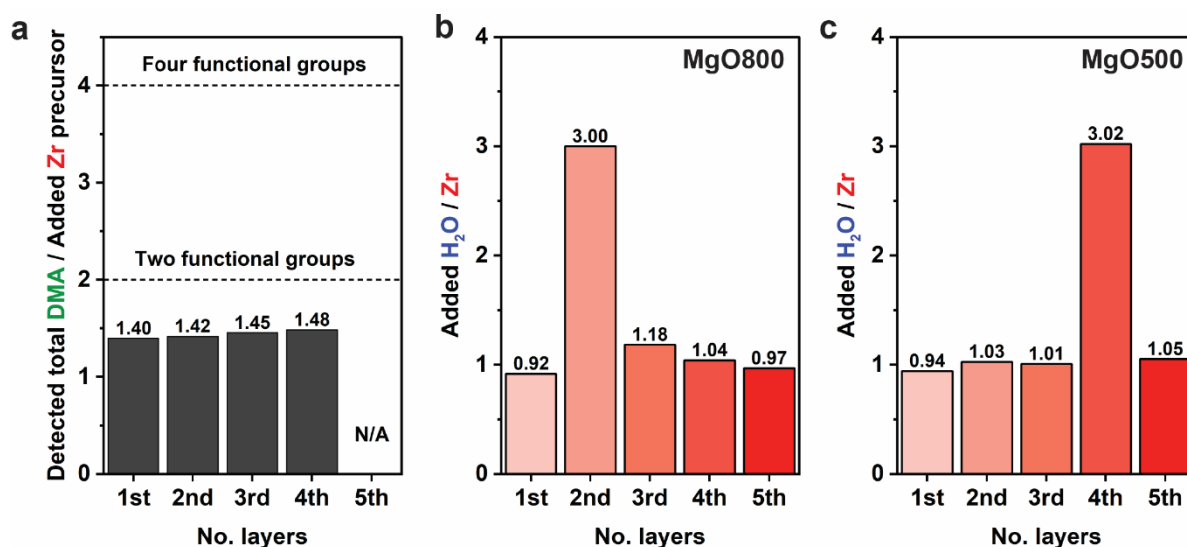


Supplementary Figure 3. Schematics describing the re-hydroxylation of the MgO support occurring in gas-phase ALD. (1) Introduction of Zr precursor; (2) Purge with counter-reactant to hydroxylate the functional group of Zr precursor. In this step, the re-hydroxylation of MgO can take place; (3) Introduction of Zr precursor for the 2nd layer deposition.



Supplementary Figure 4. Summary of the surface saturation points estimated by titration with different metal precursors and supports.

Supplementary Note 3: The quantity of deposited Zr for the first layer (204 μmol/g) was much less than the density of hydroxyl groups (622 μmol/g) measured by Grignard titration, indicating that the Zr precursor could not access all the surface OH groups presumably due to the bulky ligands. For the 2nd layer, the quantity of deposited Zr decreased by half compared to the first cycle and slightly increased up to the 5th layer indicating that not all clusters formed five full layers. The as-prepared catalyst with five layers of ZrO_x was denoted as MgOZrO₂. When Zn or Cu atoms were deposited on the ZrO_x cluster as described in [Supplementary Fig. 6](#), 200.4 μmol/g of Zn were deposited on MgOZrO₂ (Zn/MgOZrO₂) whereas 90.6 μmol/g of Cu were deposited (Cu/MgOZrO₂).

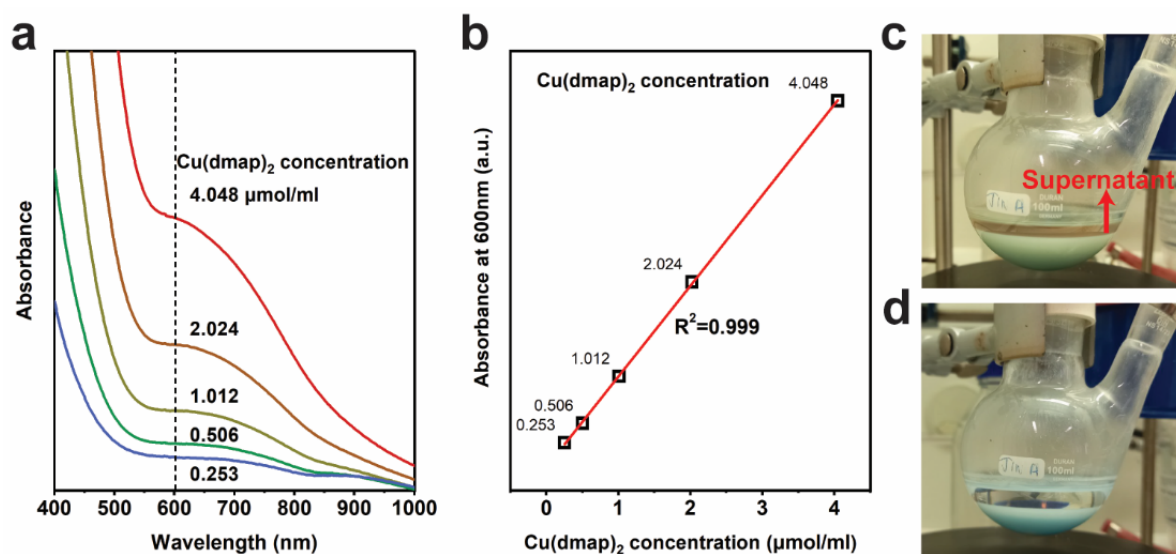


Supplementary Figure 5. (a) The ratio of the detected total DMA in the gas and liquid phases to the quantity of added Zr precursor and the ratio of added H₂O to Zr at each layer on (b) MgO800 and (c) MgO500.

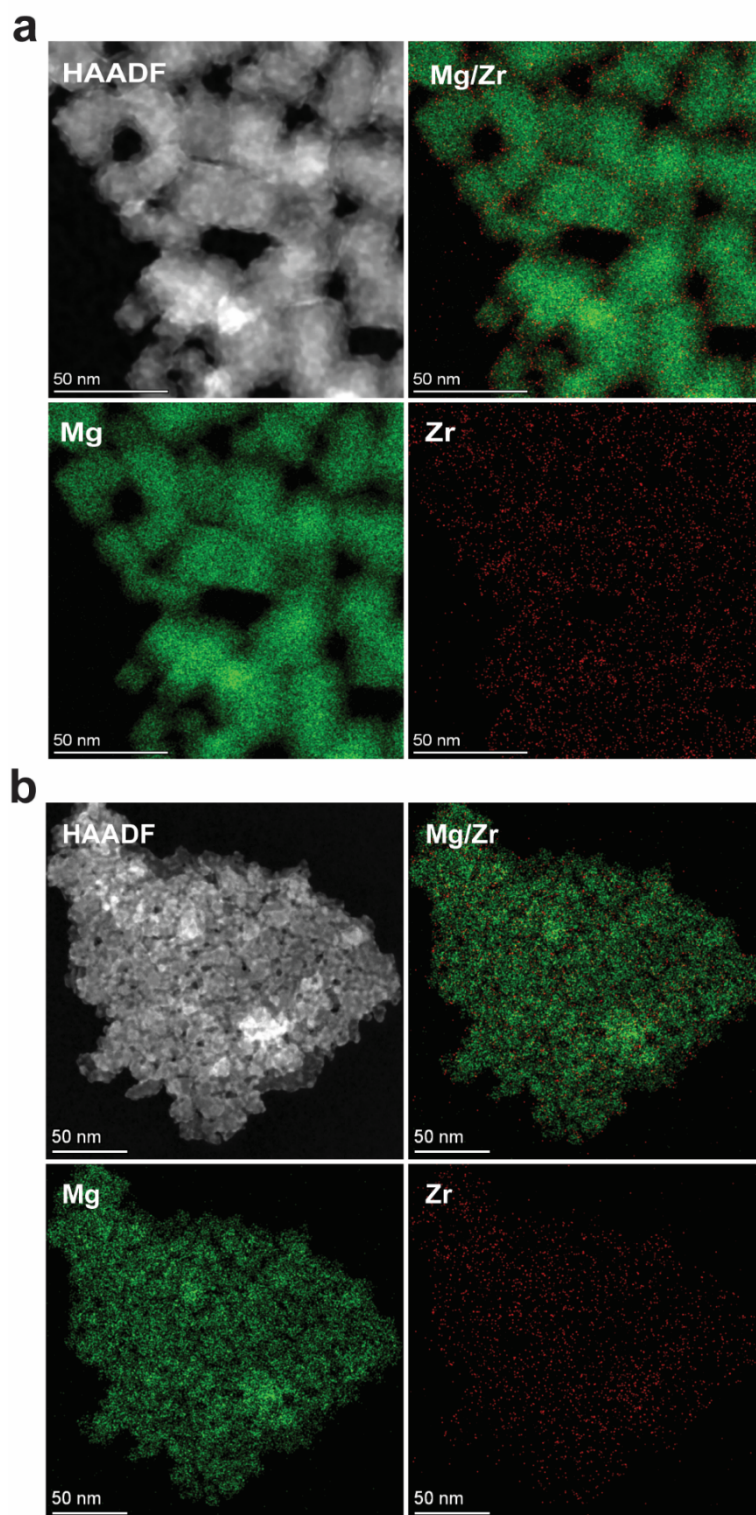
Supplementary Note 4: The dashed lines in [Supplementary Figure 5a](#) indicates the ratios of DMA to Zr precursor when two or four functional groups in Zr precursor react. If all the functional groups react, the ratio of detected total DMA amount to added Zr precursor should be 4. The discrepancy between the detected and predicted ratios might result from the adsorption of DMA on the hydroxyl group generated on the Zr atom via conjugate acid-base formation between Brønsted acid site and the amine as explained in the main article.

We suspect that the OH group resulting from H₂O titration immediately caused DMA adsorption, resulting in a reduced amount of detected DMA during this half cycle. As expected from this hypothesis, except for the 4th layer, only one ligand of the Zr precursor reacted with the surface hydroxyl group upon deposition. Subsequently, another ligand reacted with an H₂O to generate an OH, while the other two ligands remained unreacted at the end of a cycle ([Fig. 2e](#)). This sequence was supported by the fact that the amount of H₂O used for each layer was nearly equivalent to the amount of the Zr precursor (i.e. with an H₂O/Zr ratio of 1 in [Supplementary Fig. 5b](#)).

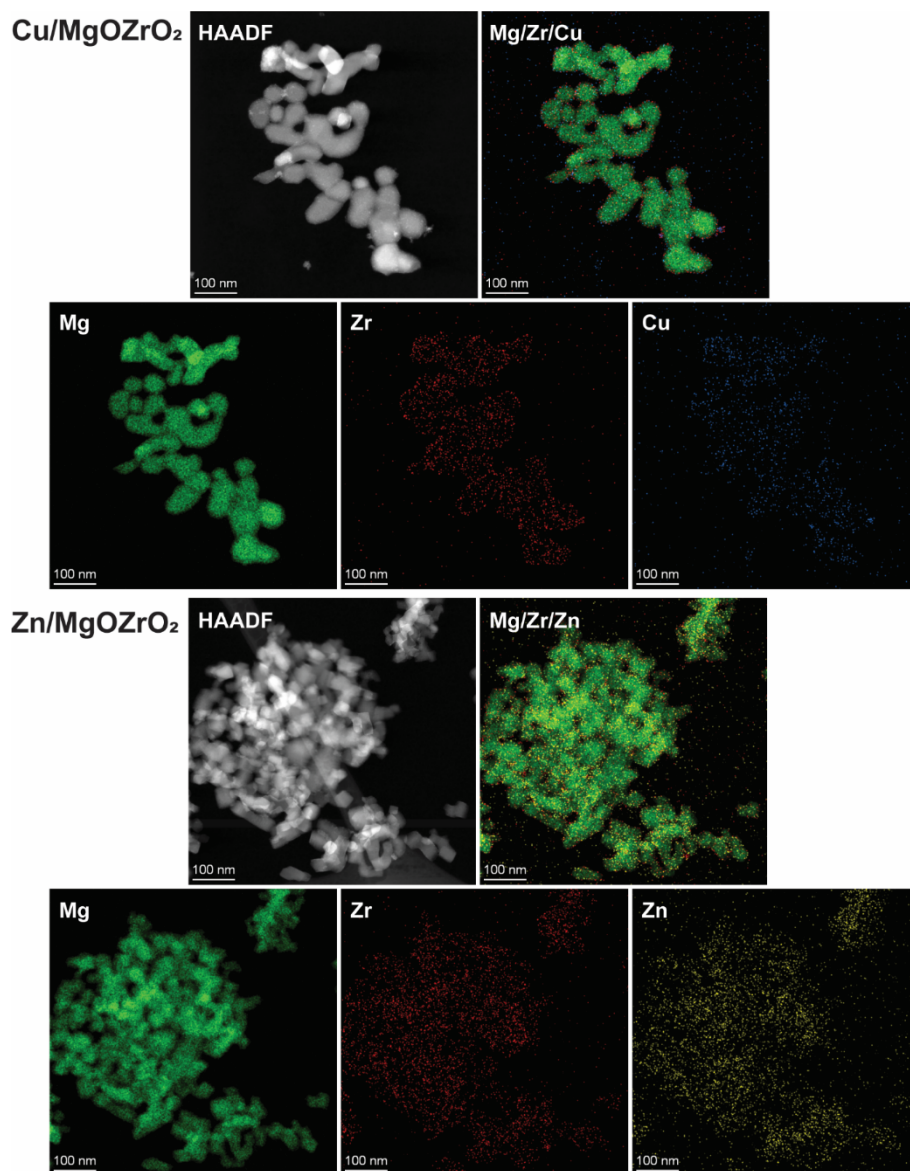
When depositing the 4th layer of Zr on MgO800, the H₂O consumed during titration was three times higher than for previous cycles and the corresponding phenomenon was also observed for MgO500 during the 2nd layer titration ([Supplementary Fig. 5c](#)). Nevertheless, the amount of produced DMA did not increase, keeping the ratio of detected DMA to added Zr precursor at 1.



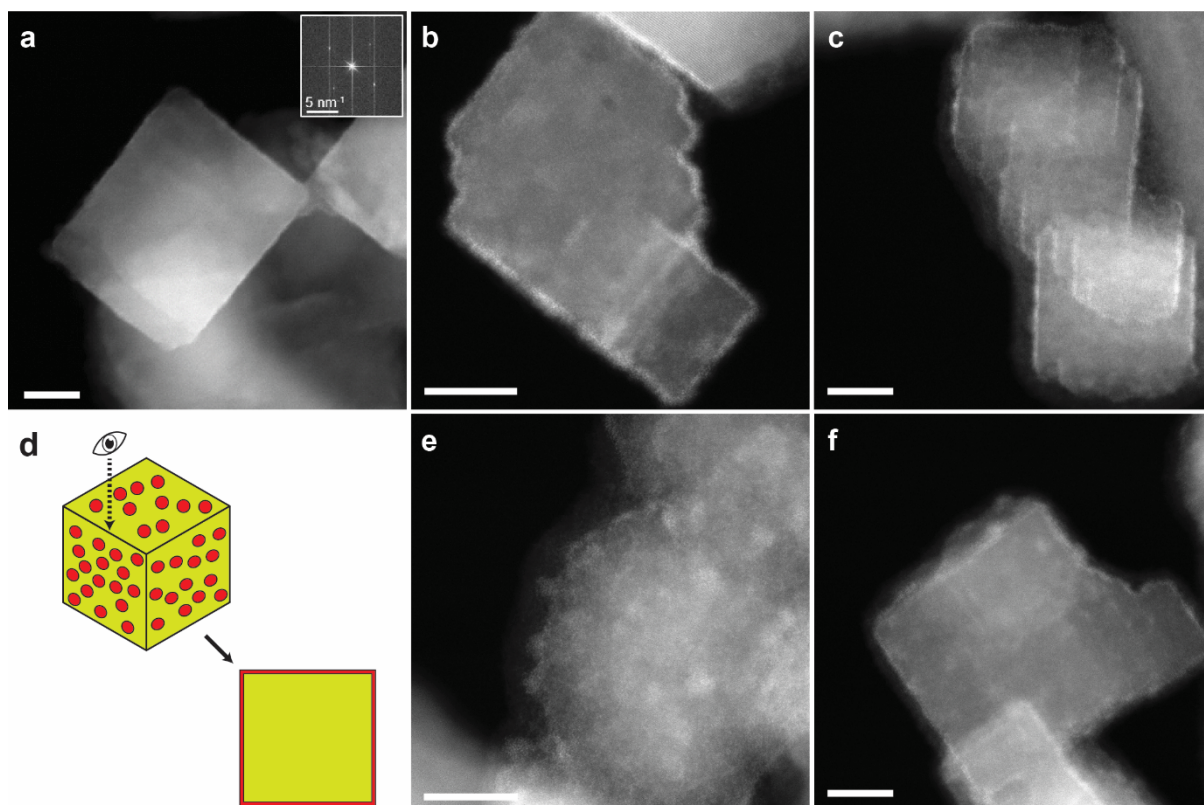
Supplementary Figure 6. (a) UV-VIS spectra of the Cu precursor in toluene with different concentrations and (b) a calibration curve of the absorbance at 600 nm versus Cu precursor concentration. Photos of supernatants after adding (c) an excess (with a brownish color) and (d) the measured stoichiometric quantity of Cu precursor (with a transparent color) on MgOZrO_2 after subsequent stirring for 12h.



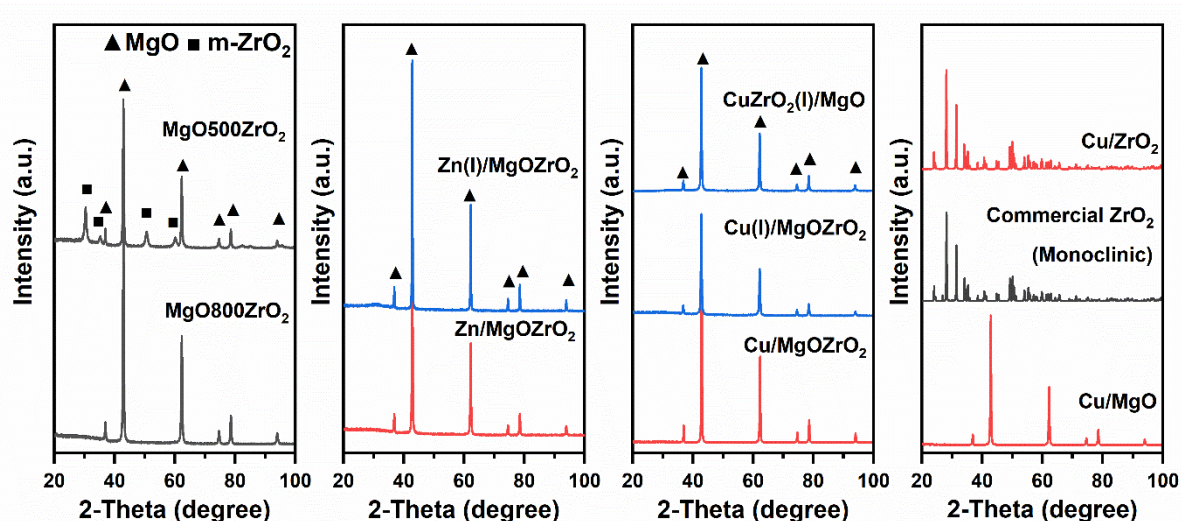
Supplementary Figure 7. HAADF-STEM image and EDX element mapping of (a) MgOZrO_2 and (b) MgO500ZrO_2 prepared by depositing five layers of ZrO_2 on MgO800 and MgO500 , respectively, using the liquid-phase ALD. ZrO_x clusters were also deposited on the MgO500 that had a higher surface area and OH density for comparison (MgO500ZrO_2).



Supplementary Figure 8. HAADF-STEM image and EDX element mapping of (top) Cu/MgOZrO₂ and (bottom) Zn/MgOZrO₂ prepared by the liquid-phase ALD. Zn/MgOZrO₂ was prepared by depositing Zn atoms on MgOZrO₂.

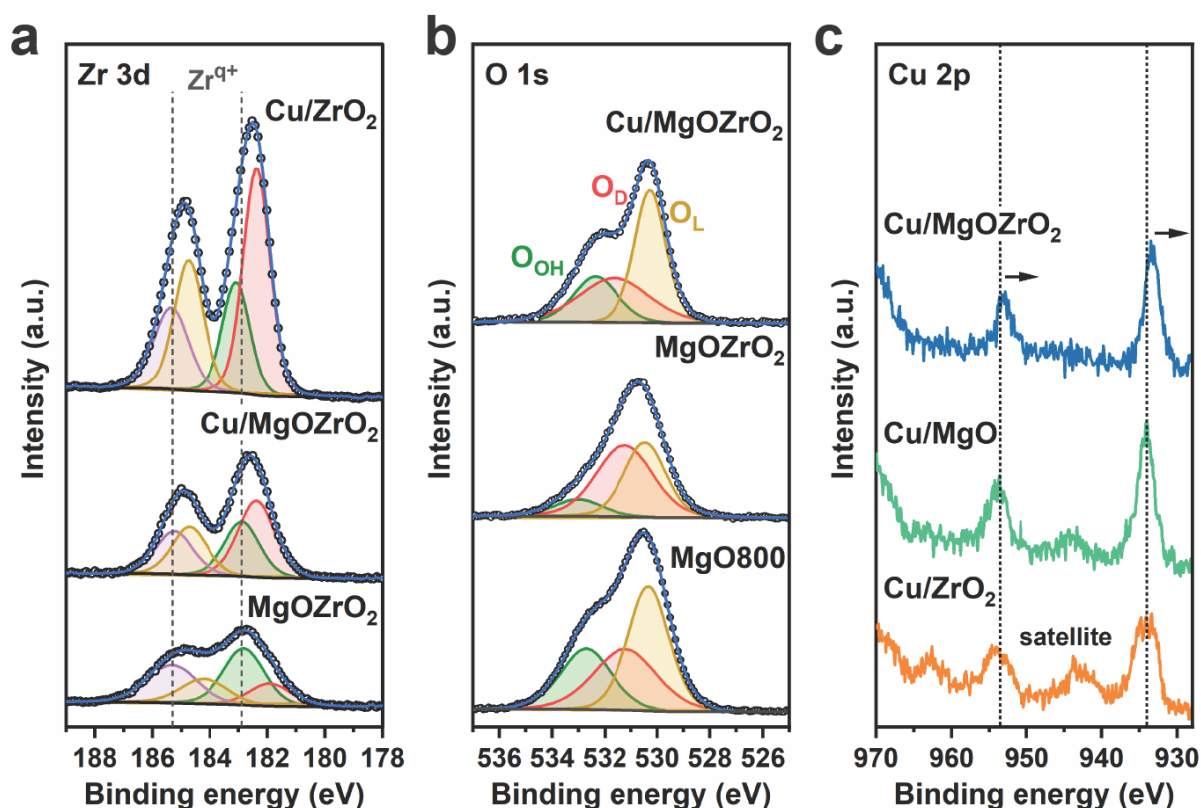


Supplementary Figure 9. AC-HAADF-STEM images of Cu/MgOZrO₂ (Scale bar, 10nm). The parts with a higher brightness in each image correspond to the position where ZrO₂ is deposited on top of MgO because of the difference in Z-contrast. (a-c) Observation of MgO cubes with an orientation parallel to the lateral surfaces of the cube makes the ZrO_x clusters on top of these {002} planes observable as a continuous layer: the projection phenomenon is detailed in (d). Inset of (a) is the local FFT showing the two orthogonal {002} set of planes at 0.22 nm. (e and f) From observation of the MgO cubes in different orientations, the cluster structure of ZrO_x on MgO surfaces could be confirmed.



Supplementary Figure 10. XRD patterns of the as-prepared catalysts. Commercial ZrO_2 used for the deposition are shown in black and the catalysts prepared by the liquid-phase ALD or impregnation are shown in red or blue, respectively.

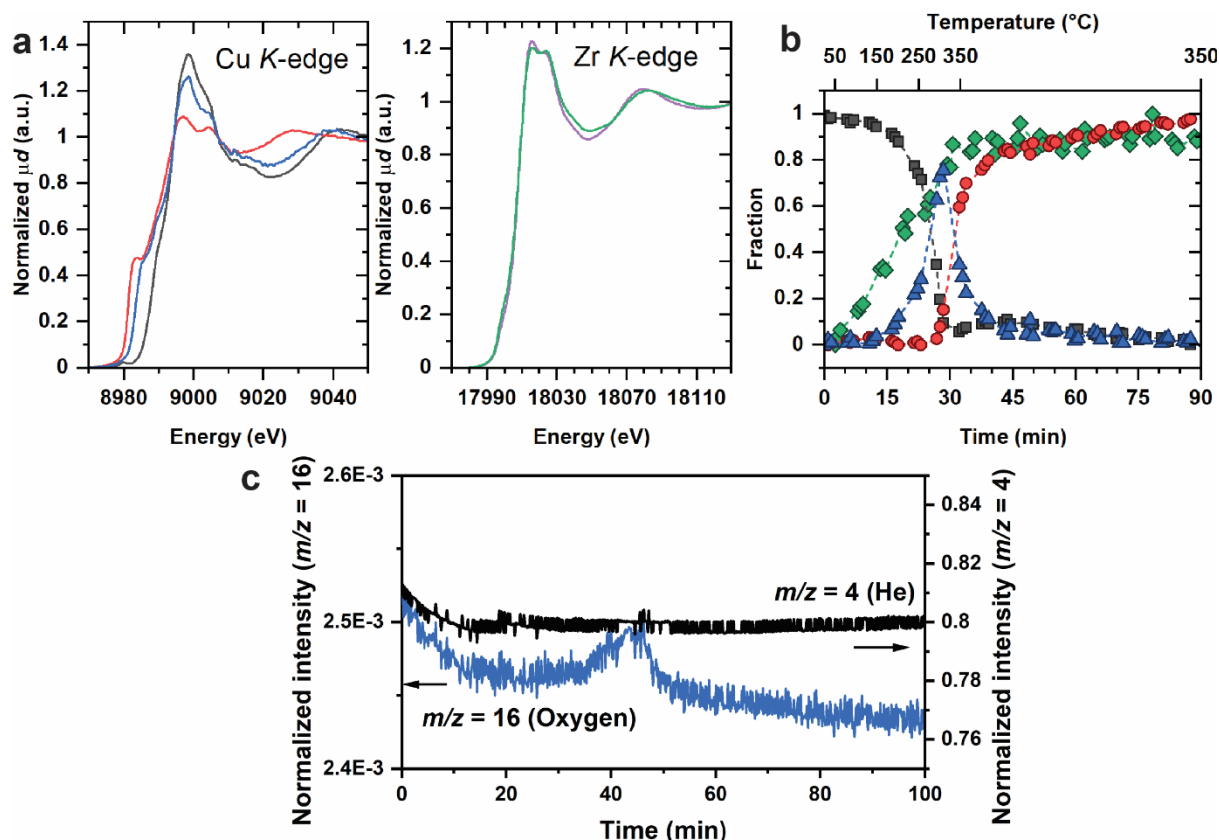
Supplementary Note 5: When comparing MgO800ZrO_2 (*i.e.* MgOZrO_2) and MgO500ZrO_2 , with five layers of deposited Zr but the different amounts of Zr due to different OH densities, the peaks corresponding to monoclinic ZrO_2 appeared in only MgO500ZrO_2 . In spite of the high ZrO_2 content (5.37 Zr wt.% in [Supplementary Table 1](#)) in MgOZrO_2 which is sufficient for detection by X-ray diffraction⁵, the absence of ZrO_2 peaks indicates the ZrO_x cluster in MgOZrO_2 were likely amorphous. In all the catalysts including Cu regardless of synthetic methods, no peaks corresponding to CuO or Cu were detected presumably due to its very low content.



Supplementary Figure 11. *Ex situ* UHV-XPS spectra of as-prepared catalysts.

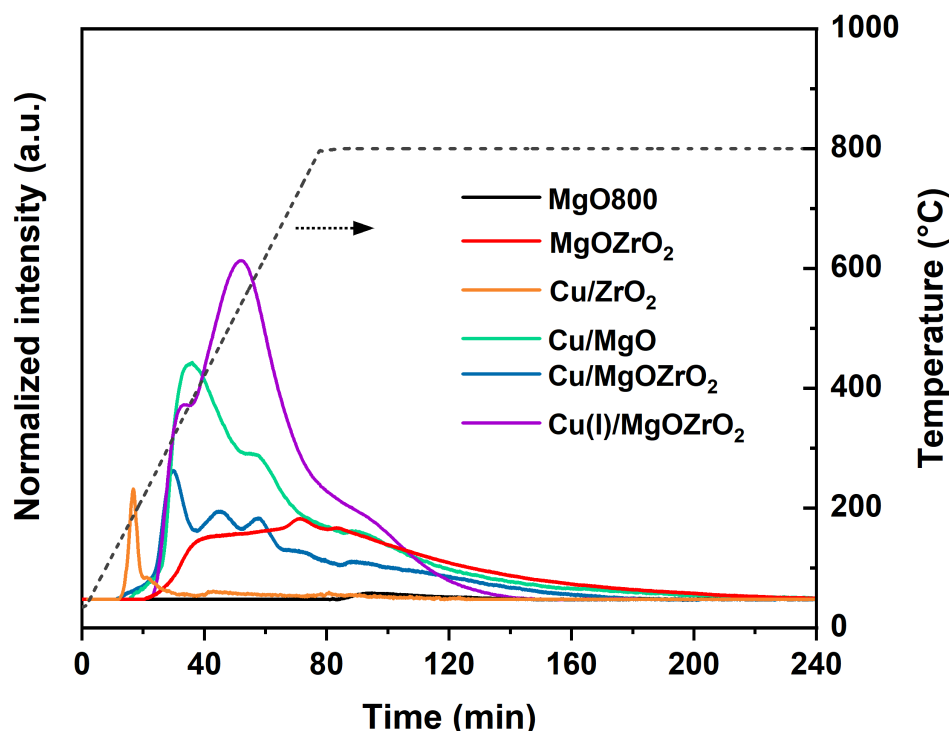
Supplementary Note 6: We performed X-ray photoelectron spectroscopy (XPS) to investigate the chemical states of O, Cu, and Zr in Cu/MgOZrO₂. The Zr 3d XPS spectrum of MgOZrO₂ revealed that Zr^{q+} ($q < 4$) accounted for 66.4% of the sample which differed from Cu/ZrO₂ that exhibited 41.2% of Zr^{q+} (Supplementary Table 2 and Fig. 11(a)). After the Cu deposition (Cu/MgOZrO₂), the proportion of Zr^{q+} substantially decreased to 44.0%, possibly resulting from the incorporation of Cu into the ZrO_x cluster. In the O 1s spectra of MgOZrO₂ (Supplementary Fig. 11(b)), the concentration of oxygen species in adsorbed OH decreased in comparison to MgO800 due to the deposition of ZrO_x cluster on OH sites, whereas the oxygen close to oxygen vacancies (O_D) considerably increased to 51.2% from 32.0% in MgO800. The increase in the content of O_D in MgOZrO₂ is consistent with the increase of the concentration of Zr^{q+}, which is indicative of an amorphous ZrO₂ cluster that is likely to possess defects^{6,7}. However, after the Cu deposition (Cu/MgOZrO₂), the content of oxygen defect species similarly decreased to 33.6 %, in line with the decrease of Zr^{q+} in Zr 3d spectra.

The Cu 2p spectra in different supports clearly showed different oxidation states of Cu resulting from the interaction with the support (Supplementary Fig. 11(c)). When the Cu precursor was directly deposited on commercial ZrO₂ (Cu/ZrO₂), the satellite peak located between 940 ~ 950 eV was obvious, indicating Cu mainly exist as the Cu²⁺ state⁸. However, Cu/MgO, where MgO800 possesses abundant amount of lower coordinated Mg_{3C}, showed the weak satellite as indicative of Cu¹⁺. Considering the peak location at 934.1 eV in Cu 2p spectra of Cu/MgO, the oxidation state of Cu in Cu/MgO seems to be between Cu¹⁺ and Cu²⁺. Therefore, it was clear that the oxidation state and the electron density of Cu was affected by its direct contact with Mg_{3C}. Interestingly, Cu/MgOZrO₂ showed the most pronounced peak shift to 933.15 eV and no satellite peak was present even in the absence of reduction of the catalyst before the XPS measurement. This result indicated that the oxidation state of Cu was more reduced in this catalyst than the Cu in Cu/MgO. The unique oxidation state of copper in Cu/MgOZrO₂ is further discussed in Supplementary Fig. 12.



Supplementary Figure 12. Cu and Zr K-edge XANES spectra (a) of independent species obtained from MCR analysis and their concentration profiles (b) for Cu/MgOZrO₂ during the temperature ramping under He flow. (c) MS profiles of $m/z = 4$ and 16 detected during the calcination.

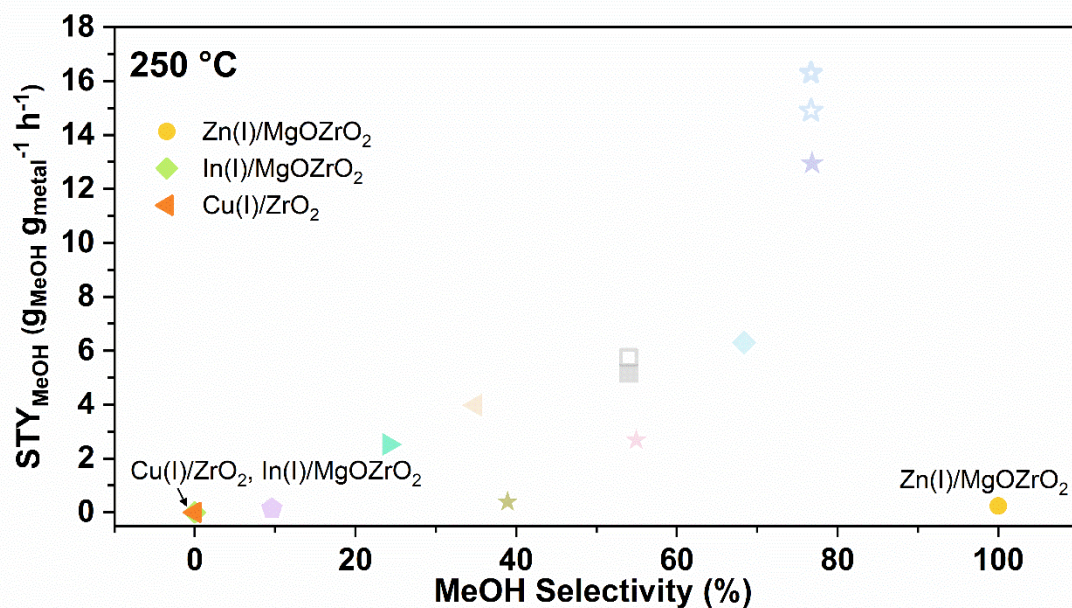
Supplementary Note 7: Changes in Cu and Zr K-edges during the calcination of Cu/MgOZrO₂ under He flow was estimated via multivariate curve resolution (MCR) analysis of XANES data with components in [Supplementary Fig. 12a and b](#). The so-called “auto-reduction” or “self-reduction” of Cu²⁺ began at 150 °C in [Supplementary Fig. 12b](#) through the intermediate phase (blue line) under He flow. This implied that there was a release of oxygen from a nearby Cu species without any reducing agents⁹. A signal of $m/z = 16$ corresponding to atomic oxygen was detected during the temperature ramping via the online mass spectrometer ([Supplementary Fig. 12c](#)), confirming this oxygen release. The auto-reduction of Cu in ZrO_x cluster means that the oxygen surrounding Cu can be easily desorbed and accordingly evidences the formation of abundant oxygen vacancy in ZrO_x cluster upon heating under He flow.



Supplementary Figure 13. H₂-TPR profiles of as-prepared catalysts (The intensity was normalized with the weight of loaded catalysts and the catalyst was pre-treated at 350 °C before H₂-TPR)

Supplementary Note 8: Comparison of H₂-TPR profiles of Cu/MgO and Cu/ZrO₂ in [Supplementary Fig. 13](#) revealed that the interaction between Cu and MgO was stronger than that between Cu and ZrO₂, showing the higher reduction temperature for Cu/MgO. ZrO_x cluster in Cu/MgOZrO₂ showed an unique reduction properties opposed to typical H₂-TPR profiles of monoclinic or amorphous ZrO₂⁷; MgOZrO₂ consumed a considerably large amount of H₂ from around 220 °C, which might result from oxygen defects accommodated in the amorphous ZrO_x clusters as revealed from XPS ([Supplementary Fig. 11](#))⁶. In Cu/MgOZrO₂, the main reduction peak occurs at a lower temperature than with Cu/MgO but at a higher temperature than with Cu/ZrO₂. This result implies the interaction between amorphous ZrO_x cluster and deposited Cu species is weaker than the direct interaction with MgO but stronger than the interaction with monoclinic ZrO₂. The smaller area under the H₂-TPR profile of Cu/MgOZrO₂ than Cu/MgO can be attributed to oxygen species already removed during the pre-treatment due to the auto-reduction behavior mentioned earlier ([Supplementary Fig. 12](#)).

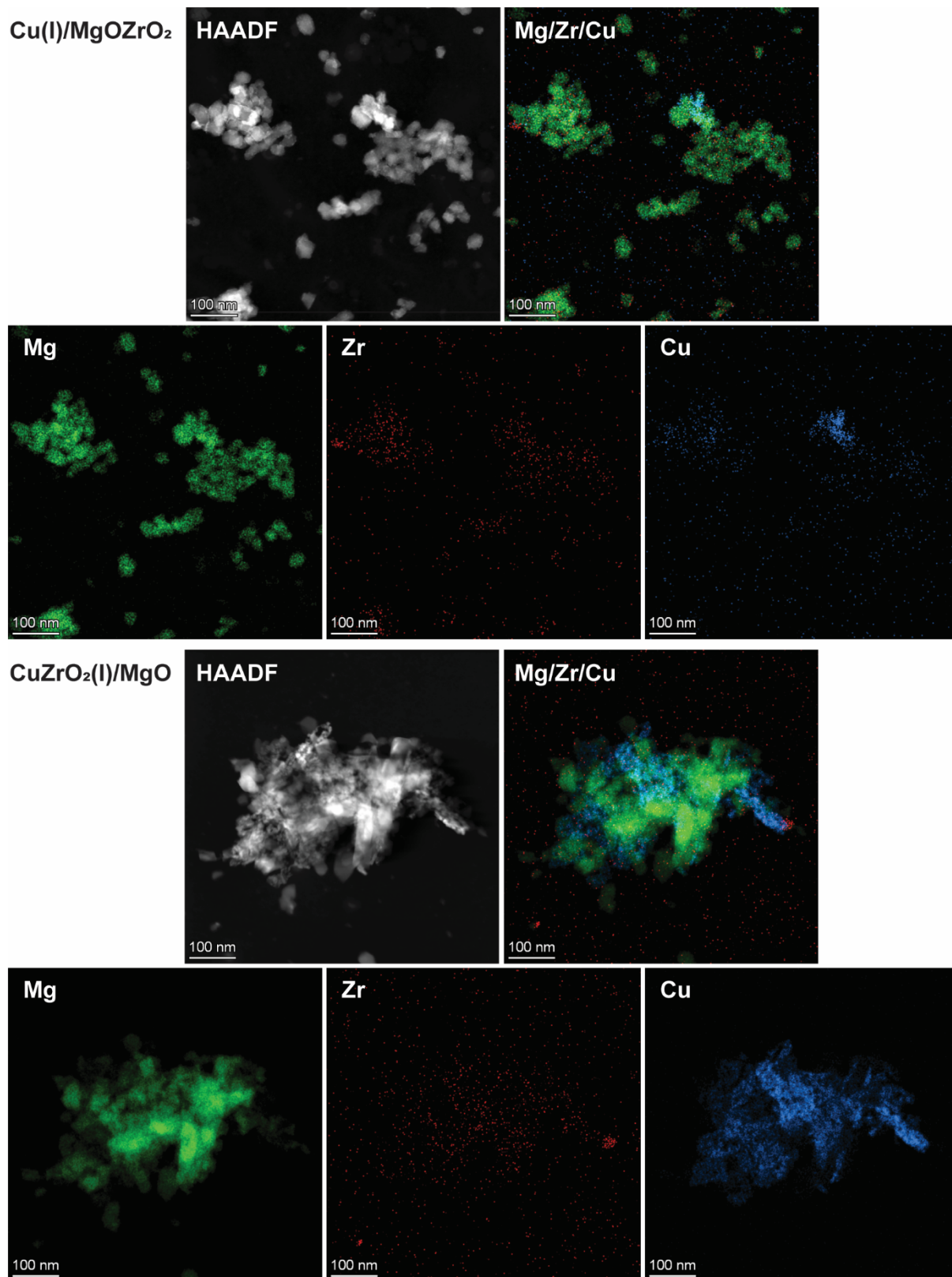
The higher reduction temperature of Cu(I)/MgOZrO₂ might result from the existence of bulk CuO as confirmed from the STEM-EDX mapping images and its high reduction temperature as reported in the literature¹⁰. Cu/ZrO₂ exhibited a sharp peak at 185 °C typically observed for the highly dispersed CuO on ZrO₂⁷.



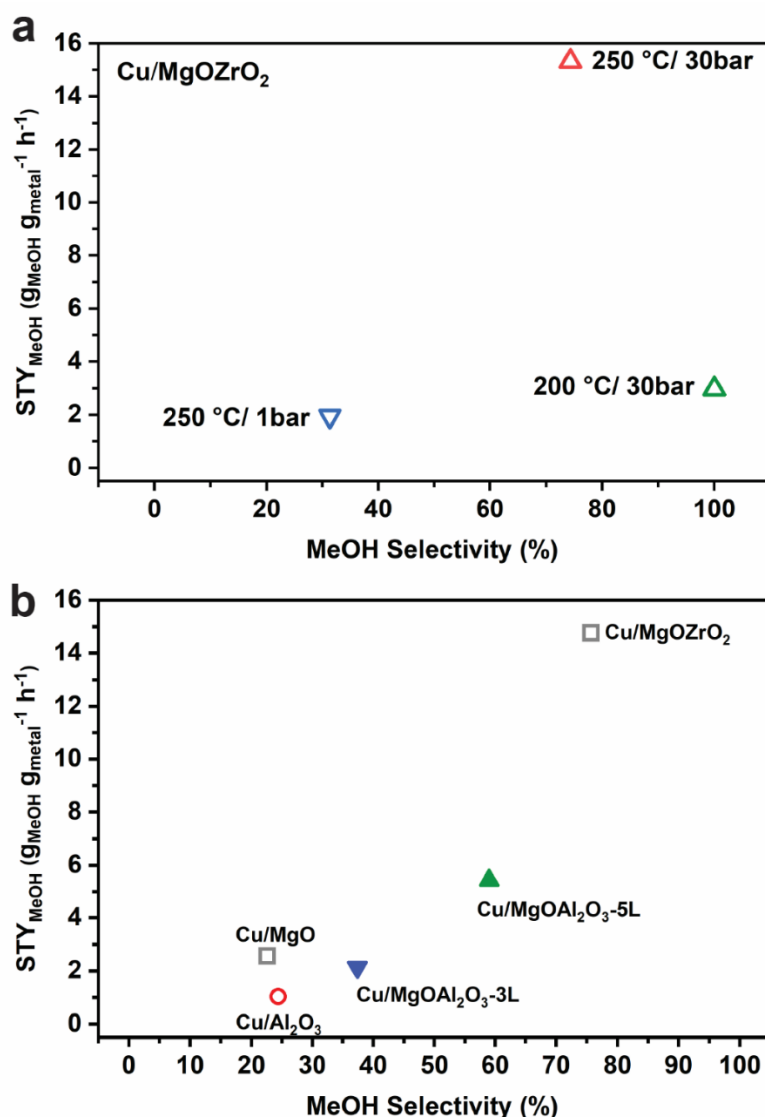
Supplementary Figure 14. Methanol selectivity and space-time yield (STY) of control catalysts prepared by the incipient wetness impregnation (the catalysts presented in the main text are with transparent symbols for comparison).

Supplementary Note 9: To preliminarily screen the most catalytically active element on MgOZrO₂ support, we initially impregnated CuO, ZnO, or In₂O₃ on MgOZrO₂ (Cu(I)/MgOZrO₂, Zn(I)/MgOZrO₂, and In(I)/MgOZrO₂). According to a preliminary screening test, we selected Cu and Zn for further exploration and these elements were deposited on MgOZrO₂ via the liquid-phase ALD method, denoted as Cu/MgOZrO₂, ZnMgOZrO₂, respectively. Cu(I)/MgOZrO₂ showed 38.9 % of the methanol selectivity and 0.39 g_{MeOH} g_{metal}⁻¹ h⁻¹ of methanol space-time yield (STY) in Fig. 3. On the other hand, Zn(I)/MgOZrO₂ exhibited 100% of methanol selectivity but the methanol STY was only 0.24 g_{MeOH} g_{metal}⁻¹ h⁻¹. In(I)/MgOZrO₂ showed no methanol production.

We tested additional control catalysts (CuZrO₂(I)/MgO, and Cu(I)/ZrO₂) prepared via incipient wetness impregnation (IWI) using similar composition as those of the catalysts synthesized via the liquid-phase ALD method (Supplementary Table 3). CuZrO₂(I)/MgO, where both Cu and ZrO₂ were impregnated via the IWI method, showed a much lower methanol selectivity and STY to 9.6 % and 0.14 g_{MeOH} g_{metal}⁻¹ h⁻¹ compared to Cu/MgOZrO₂. This can be explained by the unique and comparatively uniform structure of the Cu and ZrO_x clusters compared to the non-uniform structures of Cu, ZrO₂, and MgO on the impregnated catalysts (see images in Supplementary Fig. 15). This result highlights the synergetic effect of ZrO_x clusters combined with highly dispersed Cu atom.

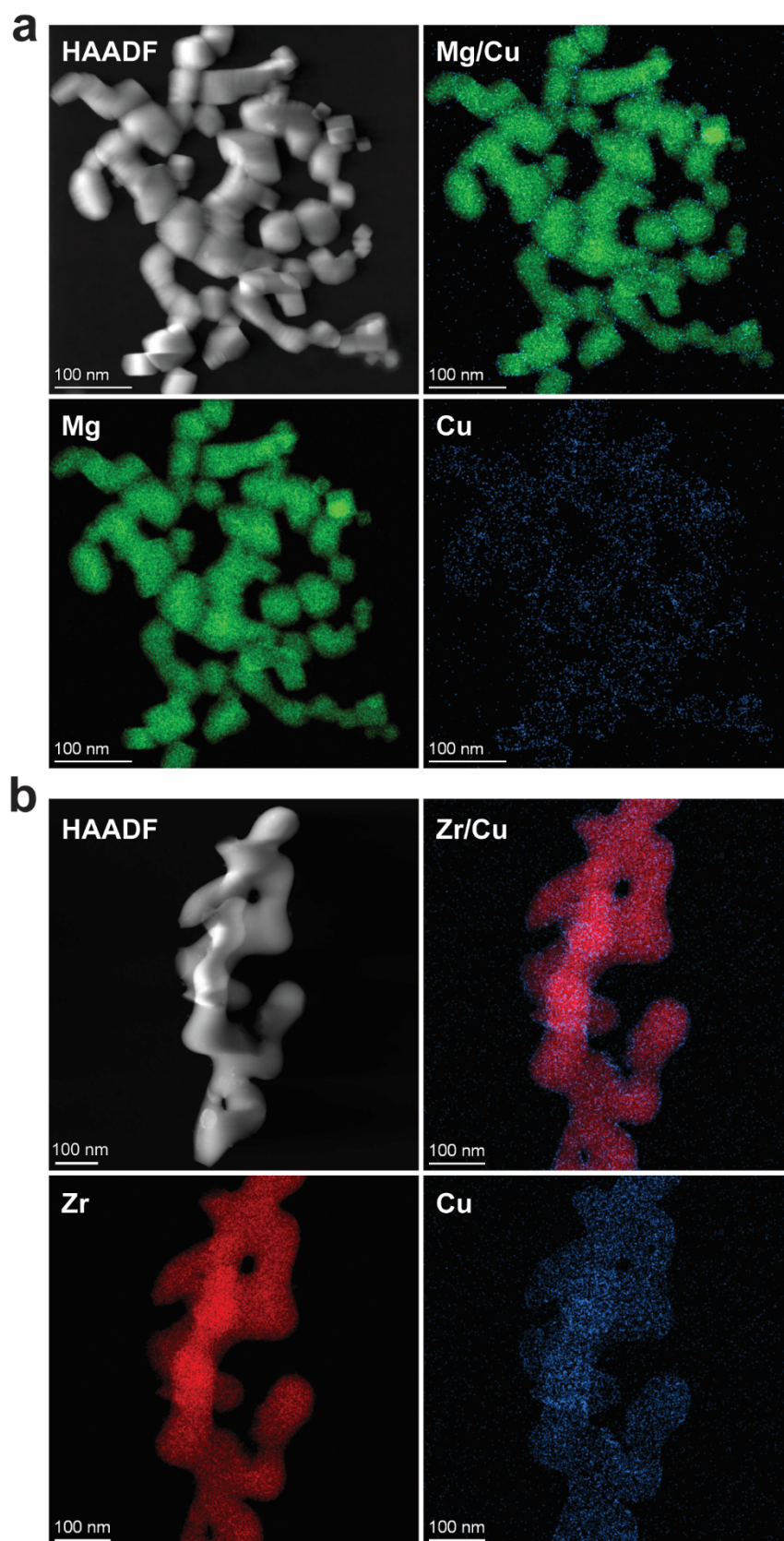


Supplementary Figure 15. HAADF-STEM image and EDX element mapping of Cu(I)/MgOZrO₂ and CuZrO₂(I)/MgO.

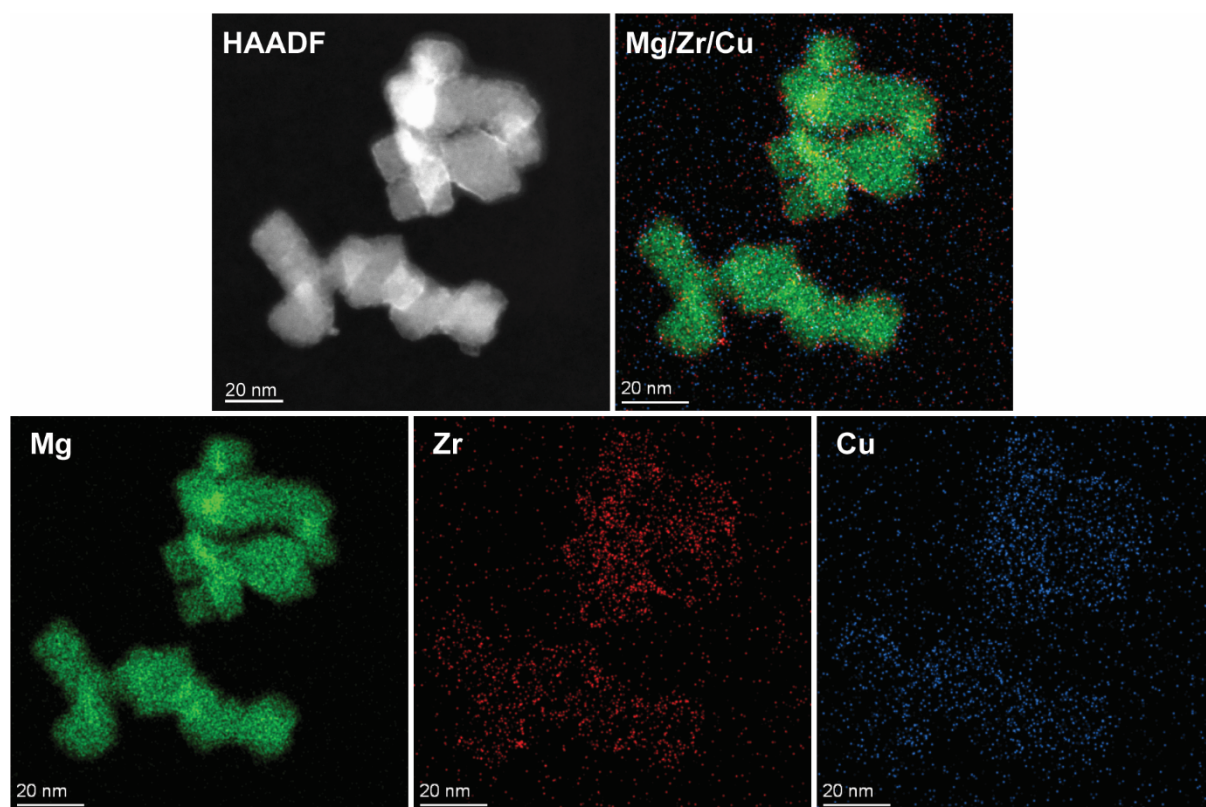


Supplementary Figure 16. Methanol selectivity and space time yield (STY) of (a) Cu/MgOZrO₂ at different temperatures and pressures and (b) Cu/MgOAl₂O₃ prepared by depositing either five or three layers of Al₂O₃ on MgO800 (Cu/MgOAl₂O₃-5L and Cu/MgOAl₂O₃-3L, respectively) followed by Cu on the top of these Al₂O₃ clusters. Cu/Al₂O₃ was prepared by directly depositing Cu using the same method on the commercial Al₂O₃

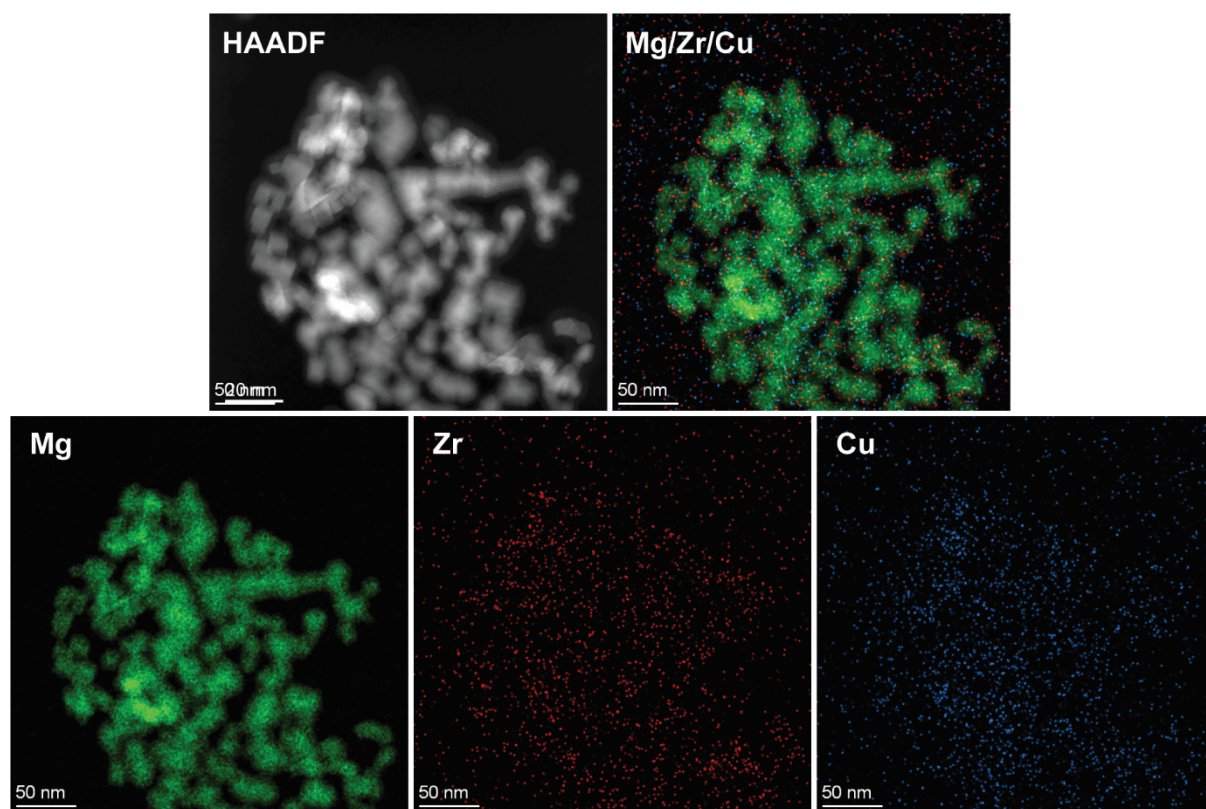
Supplementary Note 10: Cu/MgOZrO₂ was further evaluated at lower temperature and lower pressure conditions, i.e., 200 °C and 1 bar (Supplementary Fig. 16a). At the lower temperature (200 °C and 30 bar), the methanol selectivity increased to 100% and the methanol STY was 2.97 g_{MeOH} g_{metal}⁻¹ h⁻¹, which is still significantly higher than those reported in past work (Supplementary Table 4). At lower pressure (250 °C and 1 bar), both methanol selectivity and STY decreased to 31.3% and 1.95 g_{MeOH} g_{metal}⁻¹ h⁻¹, respectively. This might result from insufficient H₂ pressure to hydrogenate adsorbed intermediate species such as formate or methoxy to methanol^{11,12}. Nevertheless, a significantly enhanced methanol production activity even under mild condition when compared with past work (Supplementary Table 4) suggests that the unique Cu/ZrO_x clusters over MgO are highly active sites for CO₂ hydrogenation to produce methanol. In Supplementary Fig. 16b, Cu/MgOAl₂O₃ with Cu/Al₂O₃ clusters instead of Cu/ZrO_x clusters was also prepared and tested to verify the effect of cluster structure on the activity enhancement and compare it with the catalysts presented in the main manuscript.



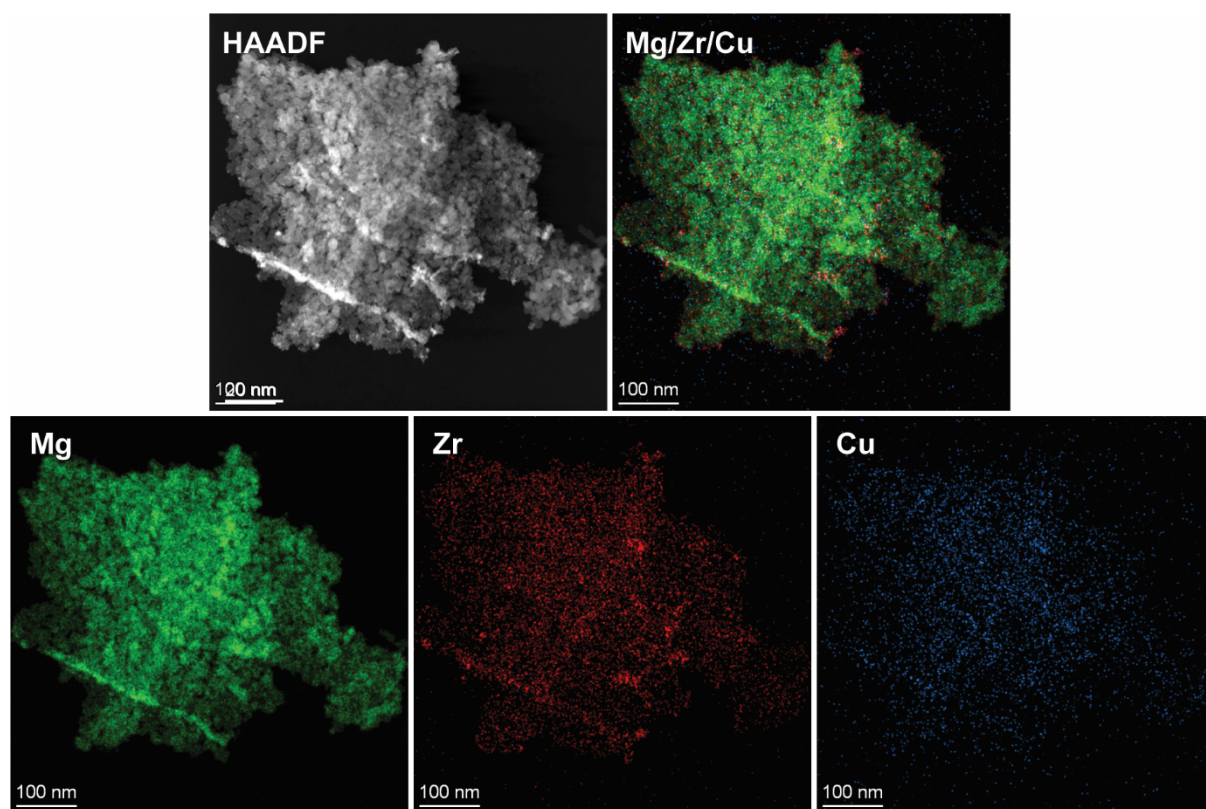
Supplementary Figure 17. HAADF-STEM image and EDX element mapping of (a) Cu/MgO and (b) Cu/ZrO₂ prepared by the liquid phase ALD.



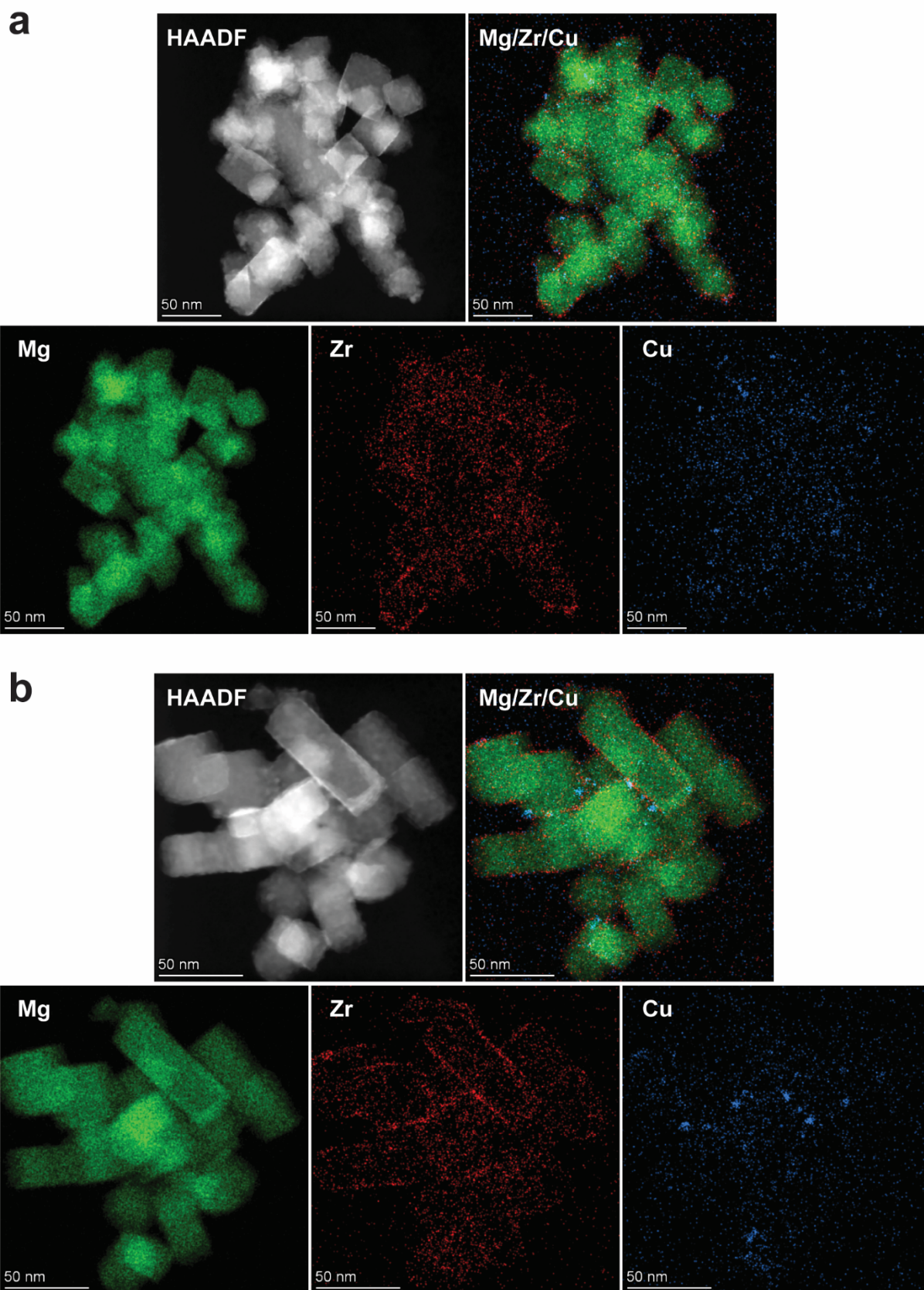
Supplementary Figure 18. HAADF-STEM image and EDX element mapping of $\text{Cu}_2\text{L}/\text{MgOZrO}_2$ prepared by the liquid phase ALD.



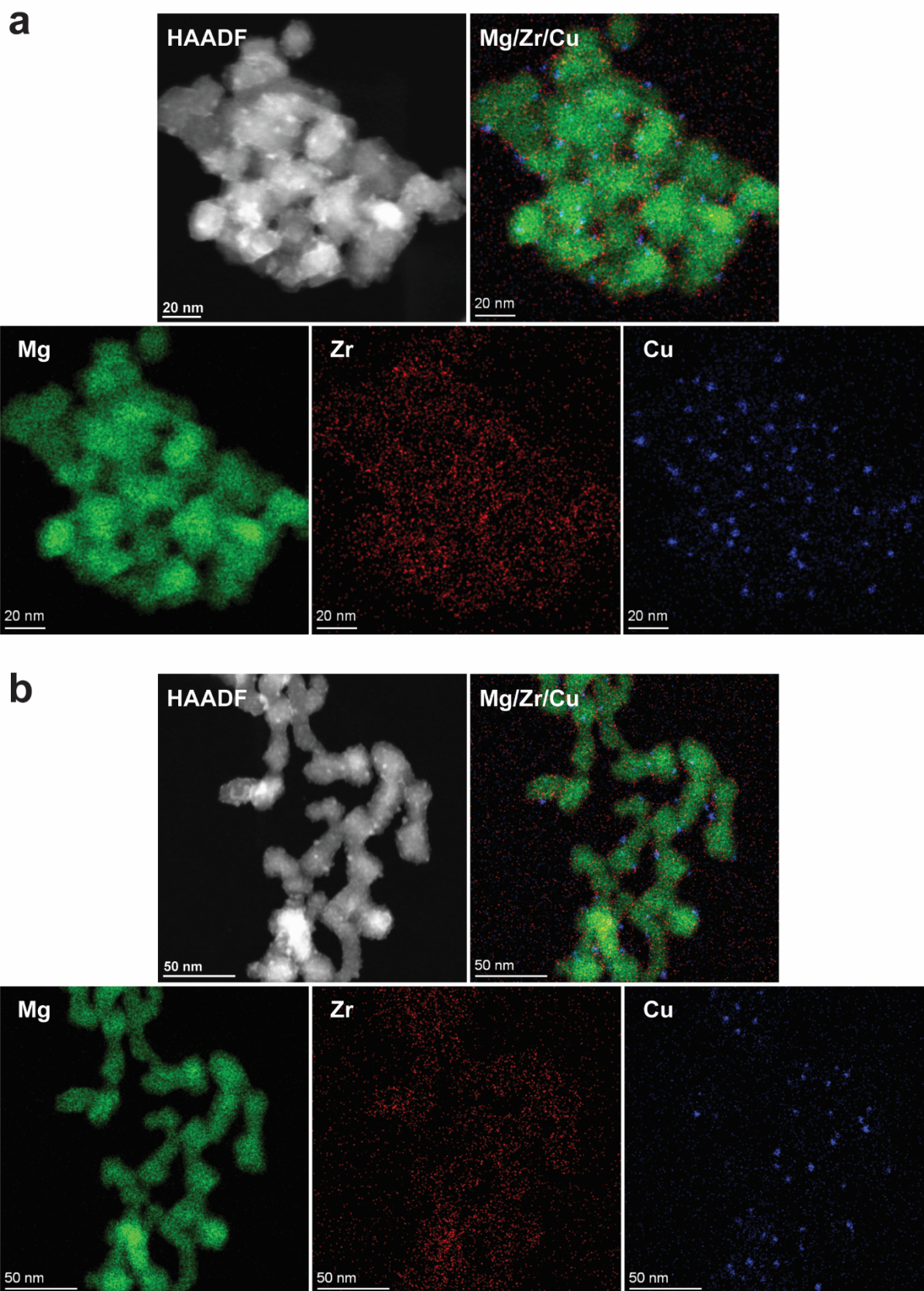
Supplementary Figure 19. HAADF-STEM image and EDX element mapping of Cu/MgOZrO₂-3L prepared by the liquid-phase ALD.



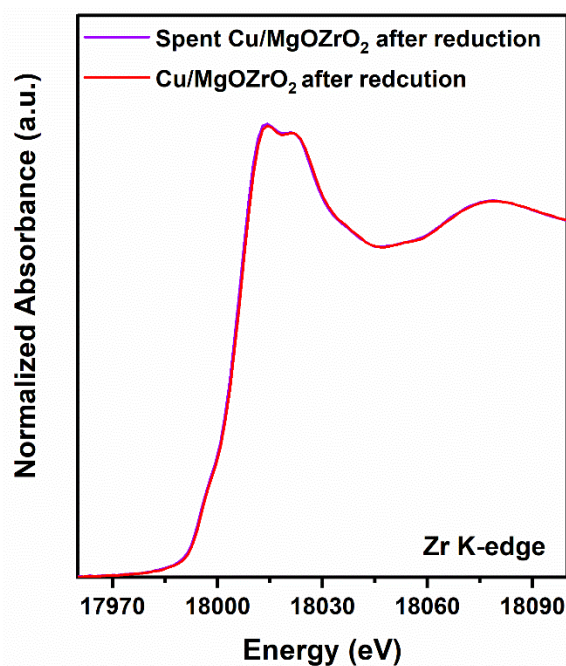
Supplementary Figure 20. HAADF-STEM image and EDX element mapping of Cu/MgO500ZrO₂ prepared by the liquid-phase ALD.



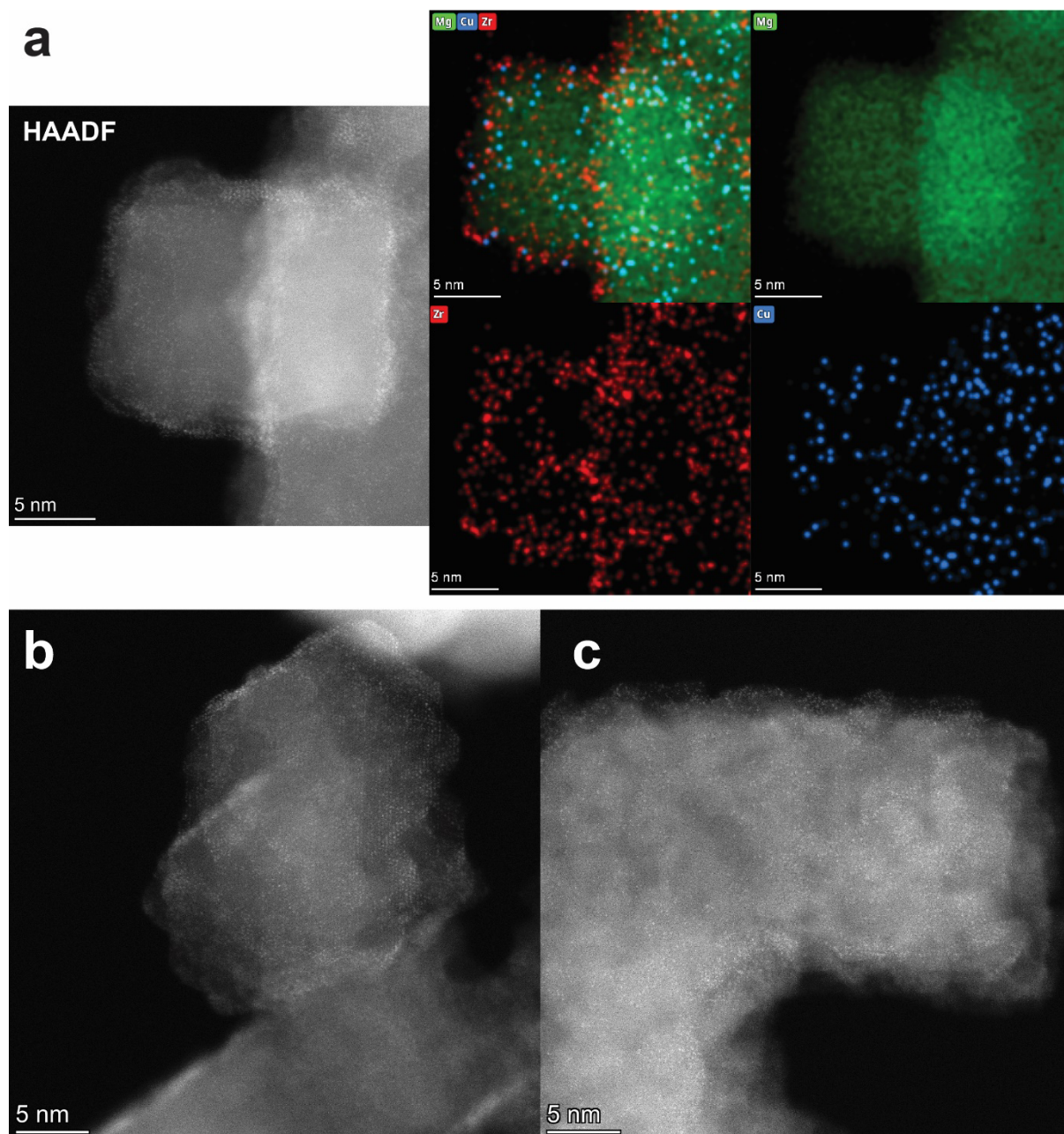
Supplementary Figure 21. HAADF-STEM image and EDX element mapping of spent Cu/MgOZrO₂ obtained at two different positions after 50 h of CO₂ hydrogenation at 30 bar and 250 °C



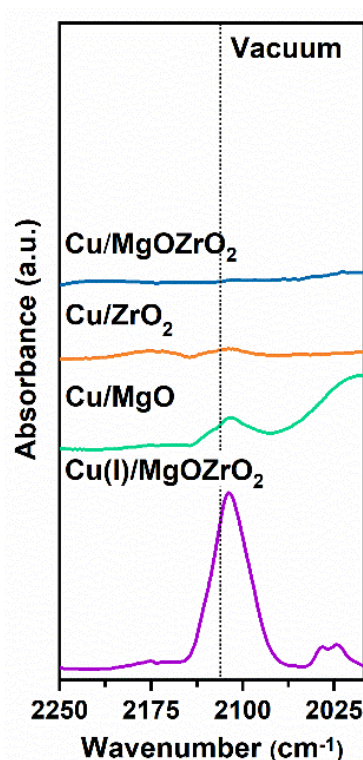
Supplementary Figure 22. HAADF-STEM image and EDX element mapping of spent $\text{Cu}_2\text{L}/\text{MgOZrO}_2$ obtained at two different positions after 50h of CO_2 hydrogenation at 30 bar and 250 °C.



Supplementary Figure 23. In situ Zr K-edges XANES spectra of fresh and spent Cu/MgOZr₂ catalysts after reduction. The spent Cu/MgOZr₂ was collected after 50h of CO₂ hydrogenation at 30 bar and 250 °C and the XANES spectrum was measured after in situ reduction.



Supplementary Figure 24. a, High-resolution HAADF-STEM and EDS mapping images of Cu/MgOZrO₂ after the reduction at 350 °C. b and c, AC-HAADF-STEM images of Cu/MgOZrO₂ after reduction at 350 °C at different positions.



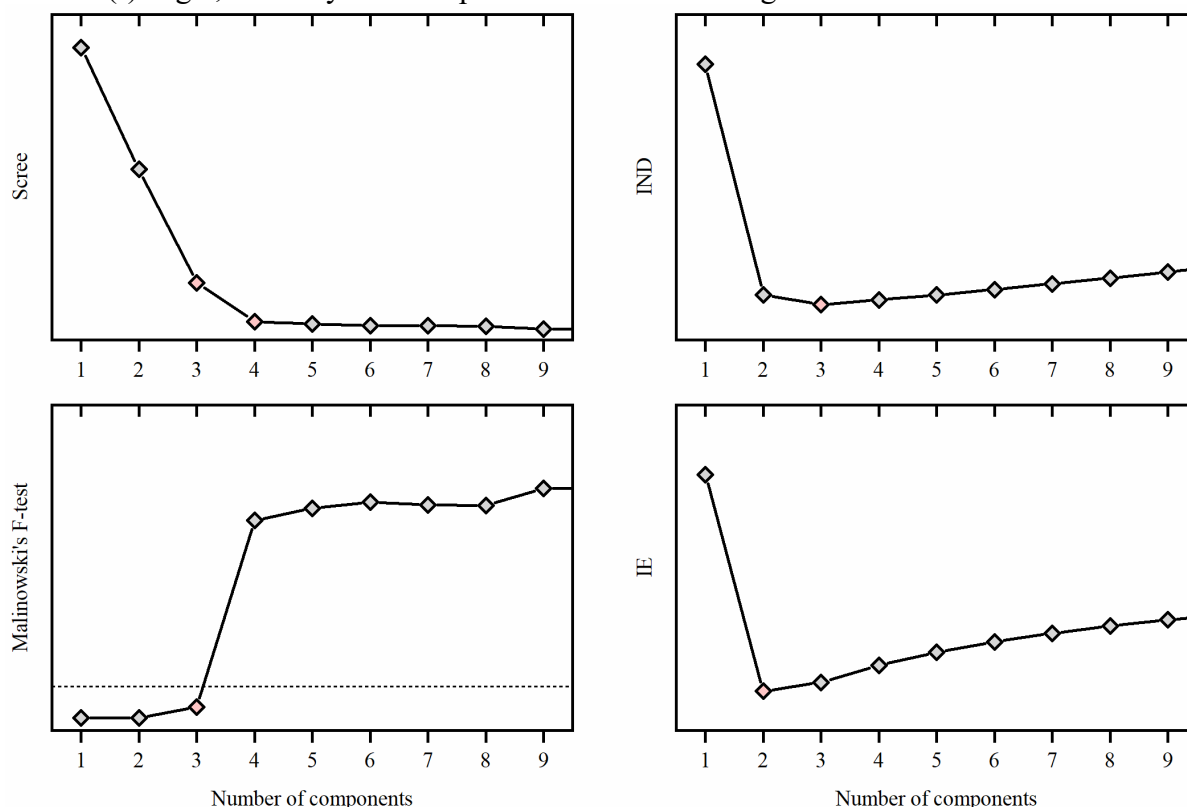
Supplementary Figure 25. In situ DRIFTS spectra obtained under vacuum after CO adsorption at 25 °C.

Supplementary Note 11: The greatest shift indicates that the back π^* antibonding is the strongest in Cu/MgOZrO₂. However, the stability of the adsorbed CO is predominantly dependent on σ bonding, which is stronger in the cation with high positive charges¹³. Therefore, in Cu/MgOZrO₂, the contribution of σ bonding is less dominant than in other catalysts. This can be explained by the electron-rich environment around Cu atom in Cu/MgOZrO₂.

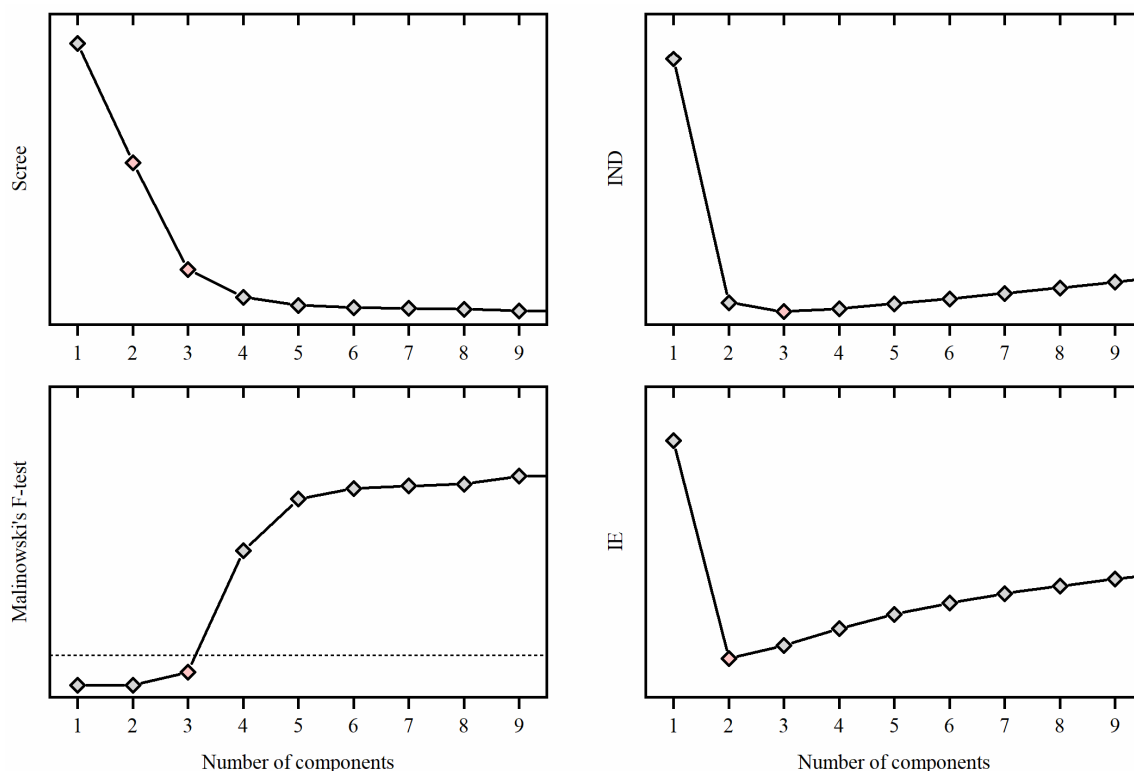
Supplementary Discussion

Supplementary Discussion 1: Principle component analysis (PCA) and Multivariate curve resolution (MCR) analyses of as-prepared catalysts

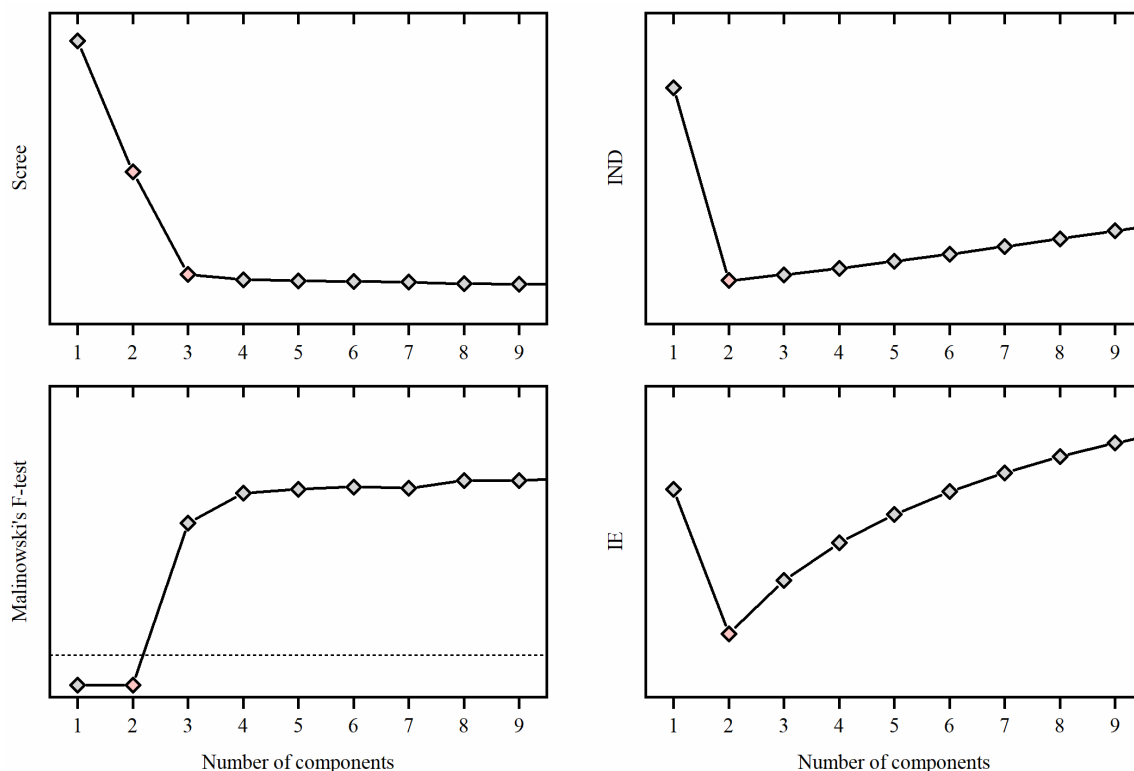
PCA and MCR analyses have been performed in PyFitIt code. In PCA, several statistical criteria were considered ([Supplementary Figs. 26-29](#)) to identify the number of independent spectra in the datasets acquired during reduction. The first criterion, Scree plot, is the variance plotted in a log-scale versus the number of components. The number of components in this case is determined near the “elbow” visually observed in the plot. For the other two criteria, i.e. the Malinowski indicator function (IND) and Imbedded Error (IE), the optimal number of components correspond to the minimum of these functions. Finally, in Malinowski F-test the number of components is considered when the values of the functions are below the 5% threshold level, which is shown by the dashed horizontal line. Simultaneous analysis of all four criteria allowed us to conclude that for Cu *K*-edge data, three independent Cu components are observed for Cu/MgOZrO₂ and Cu/MgO catalysts, and two components for Cu/ZrO₂ and CuZrO₂(I)/MgO. For the Zr *K*-edge (statistical criteria are not plotted for brevity), two Zr components were identified for all Cu-containing samples (Cu/MgOZrO₂, Cu/ZrO₂, and CuZrO₂(I)/MgO, and only one component in the case of MgOZrO₂.



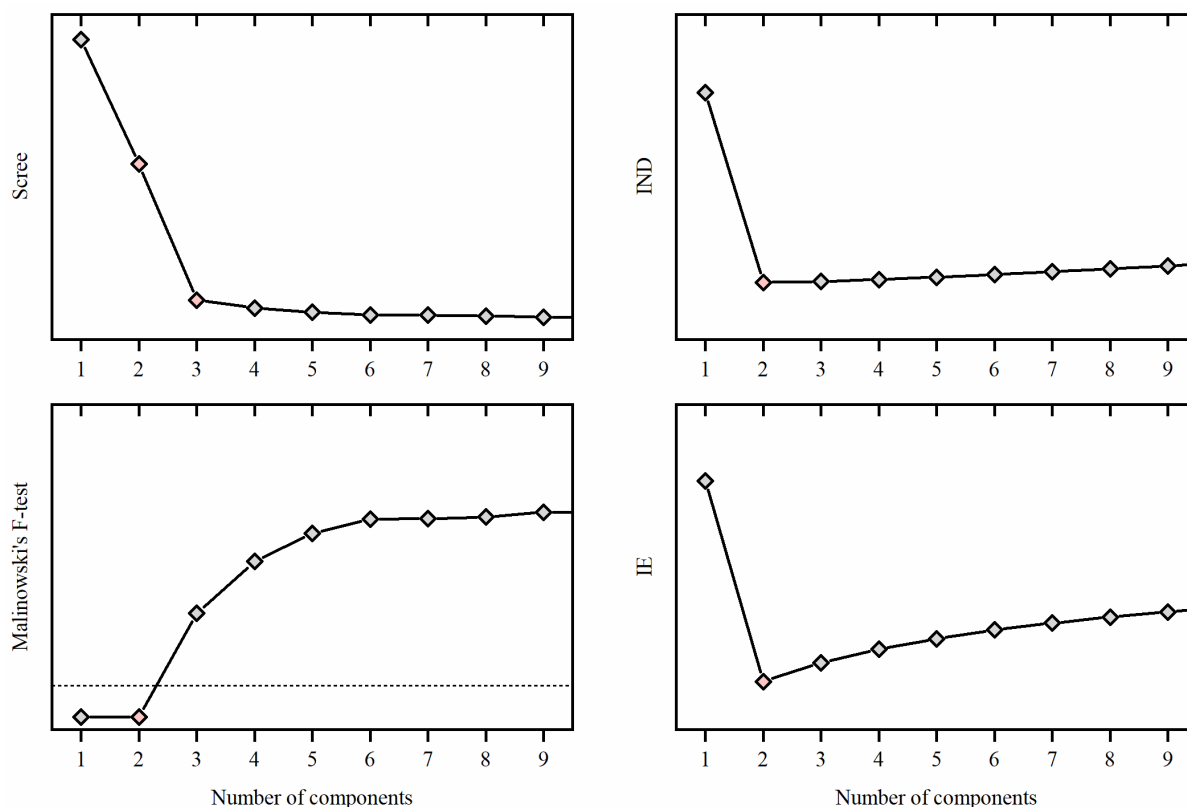
Supplementary Figure 26. Statistical criteria used to determine the number of independent Cu species from the Cu *K*-edge dataset collected upon heating of Cu/MgOZrO₂ catalyst under 10%H₂/He flow.



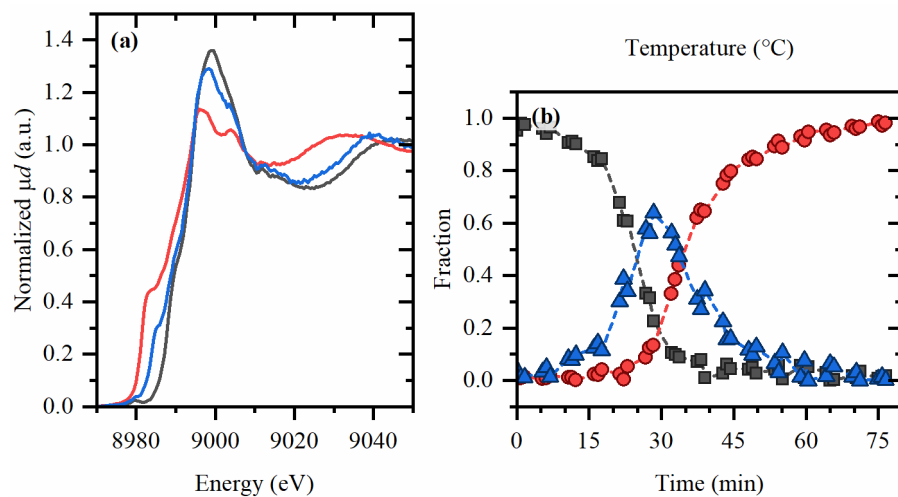
Supplementary Figure 27. Statistical criteria used to determine the number of independent Cu species from the Cu *K*-edge dataset collected upon heating of Cu/MgO under 10% H₂/He flow.



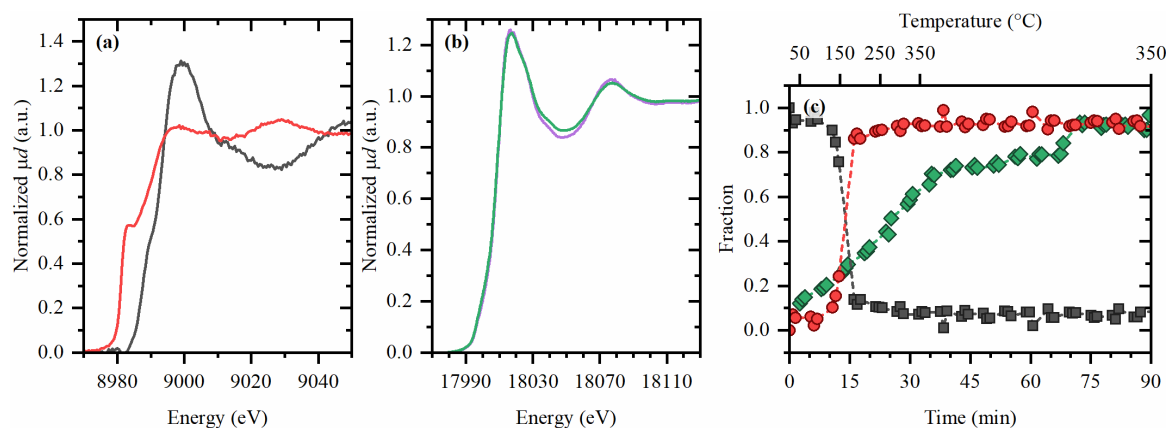
Supplementary Figure 28. Statistical criteria used to determine the number of independent Cu species from the Cu *K*-edge dataset collected upon heating of Cu/ZrO₂ under 10% H₂/He flow.



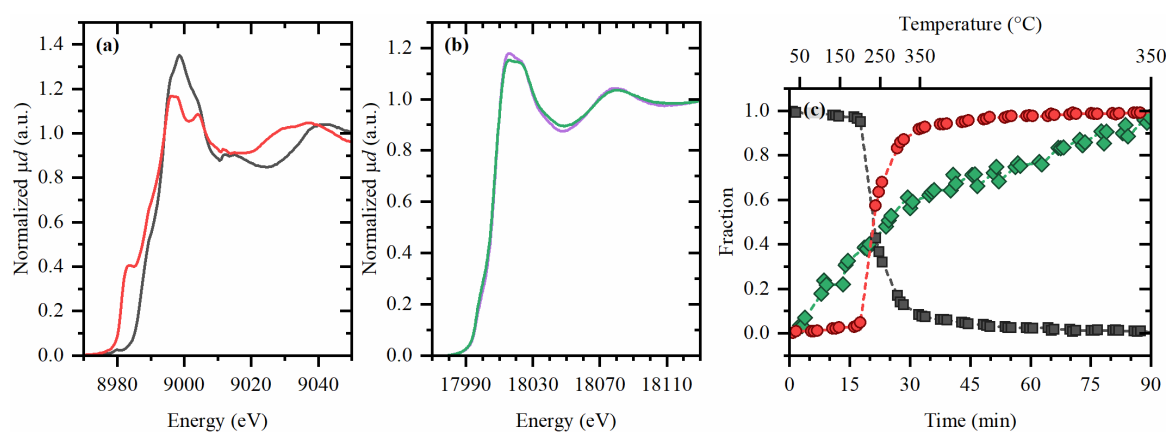
Supplementary Figure 29. Statistical criteria used to determine the number of independent Cu species from the Cu *K*-edge dataset collected upon heating of CuZrO₂(I)/MgO under 10% H₂/He flow.



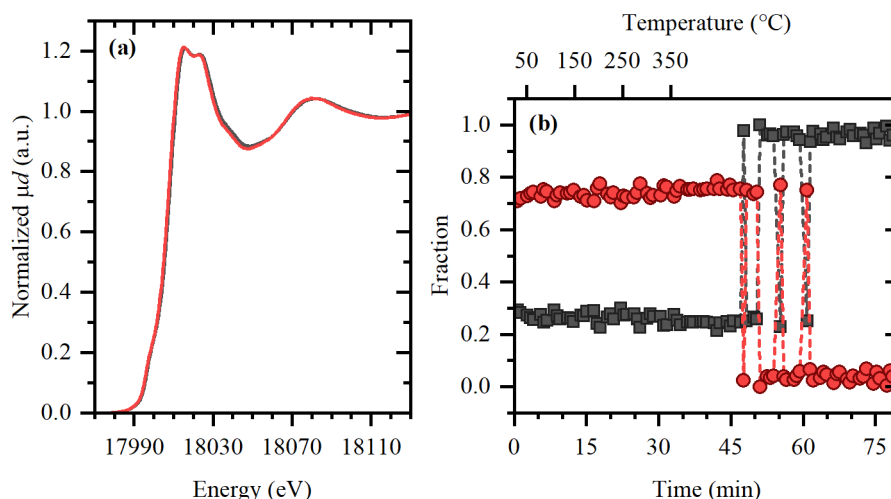
Supplementary Figure 30. Cu *K*-edge XANES spectra (a) of independent Cu species obtained from MCR analysis and their concentration profiles (b) for Cu/MgO during the reduction under 10% H₂/He flow.



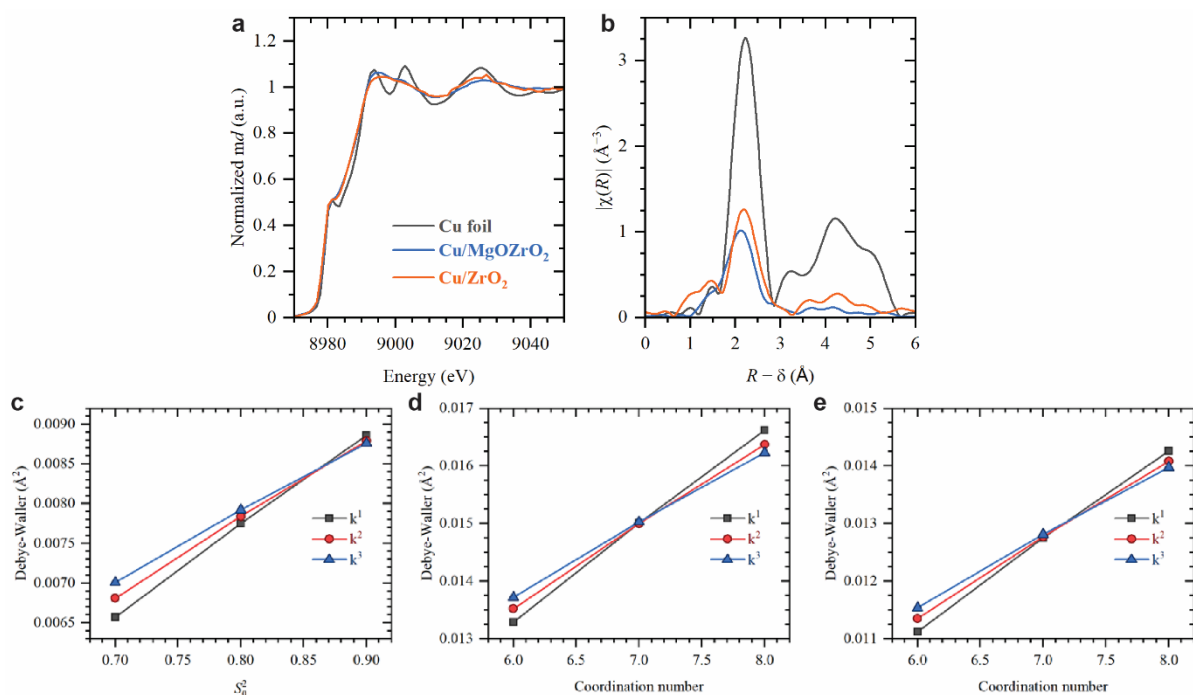
Supplementary Figure 31. Cu (a) and Zr (b) *K*-edge XANES spectra of independent Cu and Zr species, respectively, obtained from MCR analysis and their concentration profiles (c) for Cu/ZrO₂ during the reduction under 10%H₂/He flow. We note the absence of an intermediate phase as observed in Fig. 4e (see *blue curve*).



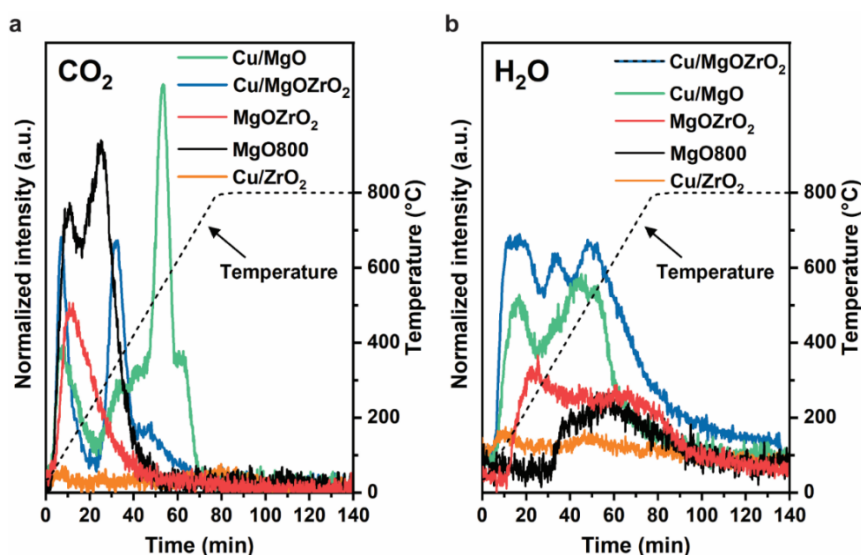
Supplementary Figure 32. Cu (a) and Zr (b) *K*-edge XANES spectra of independent Cu and Zr species, respectively, obtained from MCR analysis and their concentration profiles (c) for CuZrO₂(I)/MgO during the reduction under 10%H₂/He flow. We note the absence of an intermediate phase as observed in Fig. 4e (see *blue curve*).



Supplementary Figure 33. (a) Zr K-edge XANES spectra of independent Zr species obtained from the MCR analysis and their concentration profiles (b) for MgOZrO_2 during the reduction under 10% H_2 /He flow. During the reduction of MgOZrO_2 , only one species was observed for MCR analysis of the Zr K-edge XANES spectra, which indicates that there was no change in ZrO_x cluster structure in the absence of Cu atoms. When two components were used for the MCR analysis on purpose ([Supplementary Fig. 33a](#)), there was no change in the concentration profile during the temperature ramping as shown in [Supplementary Fig. 33b](#). The fluctuation after 45 min is an artifact of data alignment.



Supplementary Figure 34. (a) Cu K -edge XANES spectrum and (b) FT-EXAFS data of Cu/MgOZrO₂ during CO₂ hydrogenation at 250 °C and 15 bar under the reaction mixture gas flow (CO₂/H₂/He=1/3/1). (c) Debye-Waller parameters for Cu foil as function of S_0^2 for different k -weightings (d) Debye-Waller parameters for Cu/MgOZrO₂ under the reaction condition as a function of coordination numbers for different k -weightings. (e) Debye-Waller parameters for Cu/ZrO₂ under the reaction condition as a function of coordination numbers for different k -weightings. [Supplementary Figs. 34c-e](#) are presented to estimate the coordination number of Cu-Cu scattering path in each catalyst as described in [Supplementary Table. 5](#).

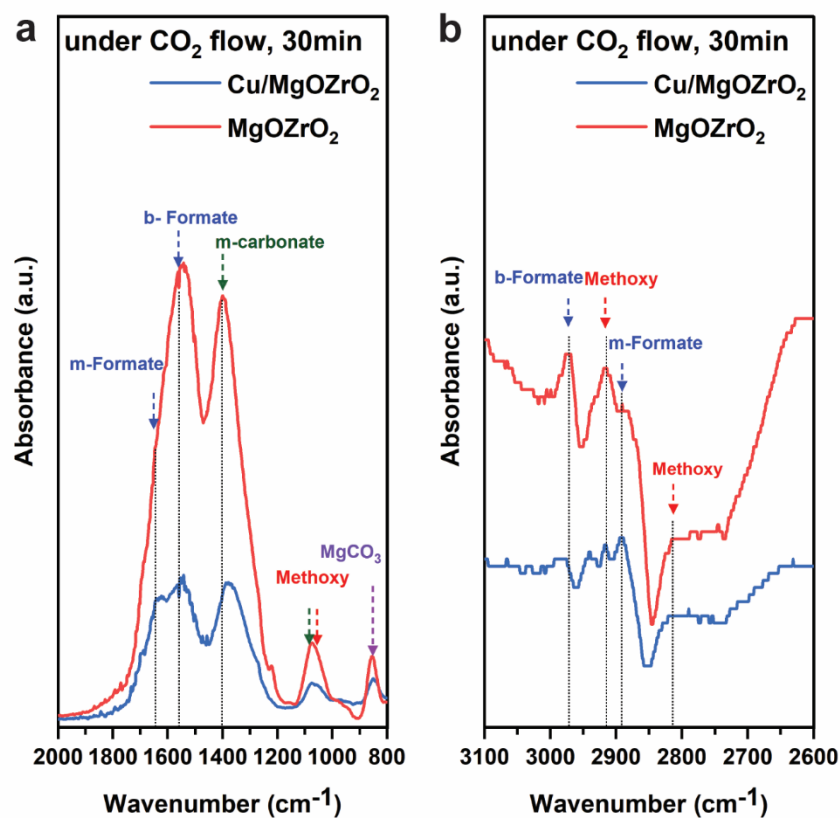


Supplementary Figure 35. Profiles of detected (a) CO_2 and (b) H_2O from CO_2 temperature-programmed desorption (CO_2 -TPD) on the different catalysts of interest.

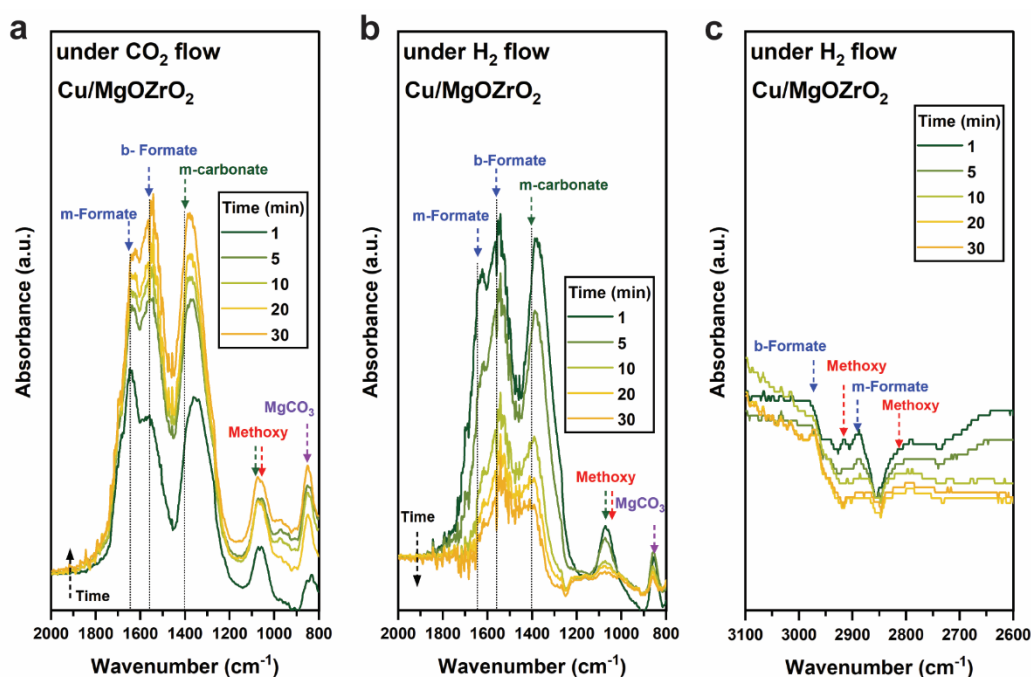
Supplementary Note 12: When performing temperature-programmed desorption (CO_2 -TPD) of MgOZrO_2 , Cu/MgOZrO_2 , Cu/MgO , Cu/ZrO_2 , and MgO800 (Figs. 5a and b and Supplementary Fig. 35), we observed that H_2O and CO_2 appeared at very different treatment temperatures depending on the catalyst. This difference was likely due to the reaction between adsorbed CO_2 and surface OH groups and the corresponding formation of formate, bicarbonate, or carboxylate species¹⁴. When comparing CO_2 -TPD profiles of MgO800 and MgOZrO_2 (Supplementary Fig. 35), we clearly saw that the deposition of ZrO_x clusters on MgO facilitated the desorption of CO_2 . In particular, the desorption peak at the high temperature observed in the profile of MgO800 disappeared and CO_2 desorption at a lower temperature accompanied the desorption of H_2O , which indicated that newly formed OH groups by ZrO_x clusters participated in CO_2 adsorption and desorption.

Cu/MgOZrO_2 with Cu/ZrO_x clusters showed two main peaks and one small peak for CO_2 desorption at 92, 347, and 501 °C, respectively. In case of H_2O desorption, the peaks in Cu/MgOZrO_2 appeared at 161, 360, and 511 °C. The simultaneous desorption of CO_2 and H_2O at 347 and 501 °C might result from decomposition of adsorbed species formed by adsorbed CO_2 and surface OH groups, whereas the sharp evolution of CO_2 at 92 °C could be mainly attributed to weakly adsorbed CO_2 . On the other hand, CO_2 desorption from Cu/MgO took place at 104, 346 (shoulder), and 547 °C while H_2O desorption mainly occurred at 195, 366 (shoulder), and 465 °C. The peaks at 104 and 547 °C are associated with desorption from weak and strong CO_2 adsorption sites, respectively, on the MgO but the broad desorption peaks of CO_2 and H_2O at 346 and 465 °C, respectively, likely result from the decomposition of adsorbed species.

Importantly, the highest CO_2 desorption temperature in Cu/MgO (547 °C) was located at a much higher temperature than in bare MgO800 (275 °C) (Supplementary Fig. 35a). In addition, the desorption of H_2O was more pronounced in Cu/MgO than in MgO800 . Those results imply that the existence of Cu promoted the participation of surface OH group on MgO in CO_2 adsorption/desorption and the resulting adsorbed species are strongly bound to the surface of Cu/MgO . We observed the identical phenomenon from comparison between Cu/MgOZrO_2 and MgOZrO_2 . The deposition of Cu on ZrO_x clusters (Cu/MgOZrO_2) led to the new CO_2 desorption peak at the higher temperature (347 °C), in comparison to the single peak at 136 °C in CO_2 desorption on MgOZrO_2 .

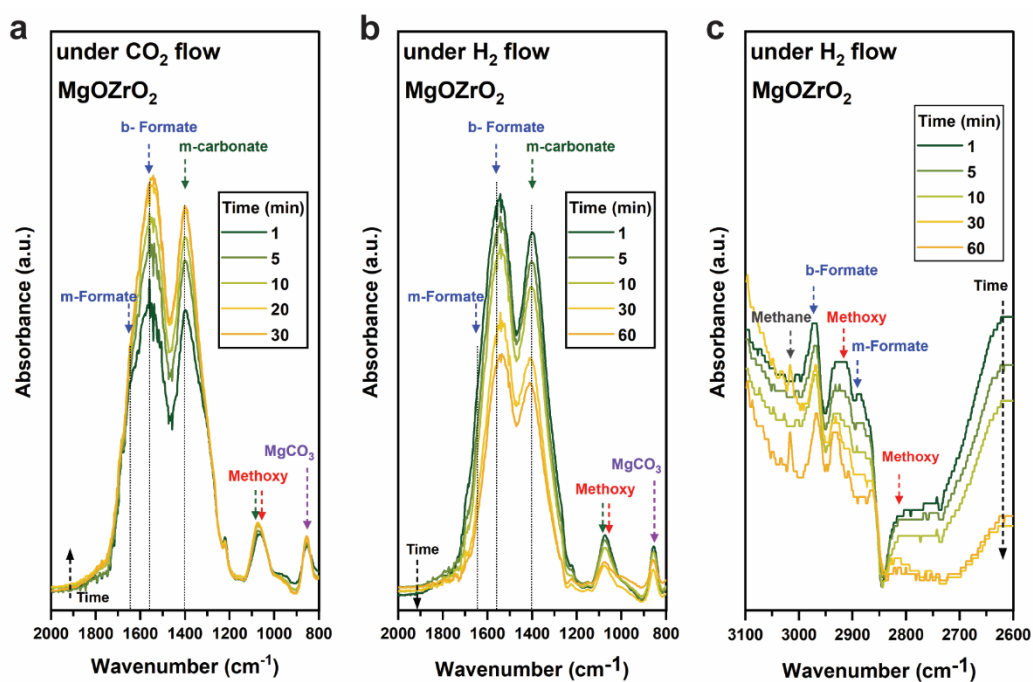


Supplementary Figure 36. In situ DRIFT spectra of Cu/MgOZrO₂ and MgOZrO₂ after 30 min under CO₂ flow at 250 °C and 1 bar in two different wavenumber ranges.

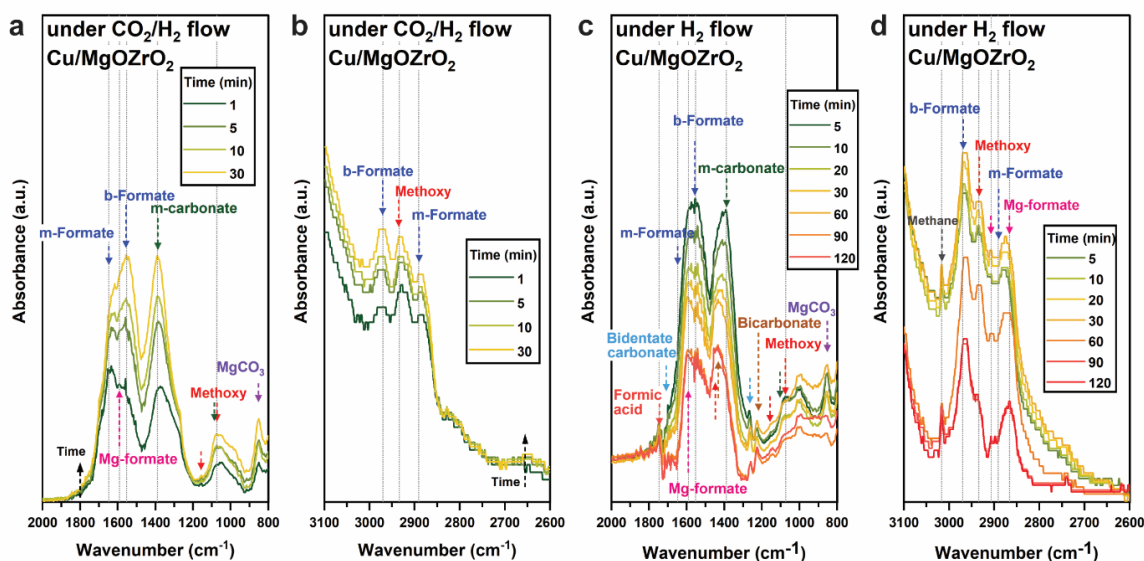


Supplementary Figure 37. Time-dependent in situ DRIFT spectra of Cu/MgOZrO₂ under (a) CO₂ and (b and c) under H₂ flow at 250 °C and 1 bar.

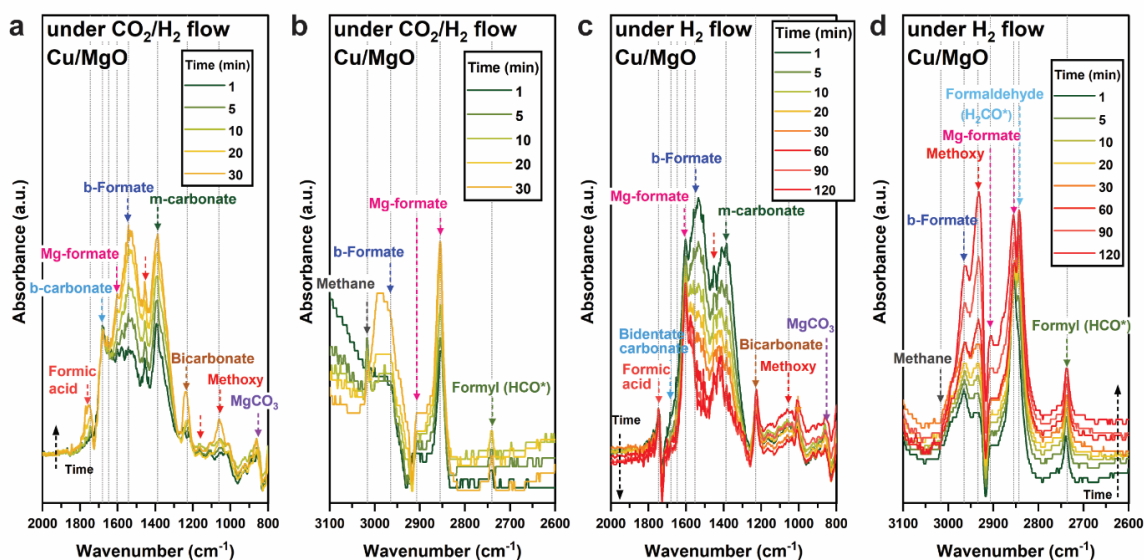
Supplementary Note 13: To investigate the nature of the CO₂ adsorbed species and their desorption behavior, we conducted adsorption and desorption experiments under CO₂ flow, and then during a following period of H₂ flow, using in situ DRIFTS. During initial CO₂ adsorption, we observed the peak corresponding to monodentate(m)-carbonate but also the peaks for monodentate(m)- and bidentate(b)- formates, and methoxy groups on both MgOZrO₂ and Cu/MgOZrO₂ even in the absence of H₂ (Supplementary Figs. 36a and b). The evolution of m-formate on Cu/MgOZrO₂ was initially faster than that of b-formate under CO₂ flow whereas, on MgOZrO₂, the b-formate was more predominant than m-formate over the entire time period (Supplementary Figs. 37a and 38a). The desorption behavior and stability of those adsorbed formates were compared by tracking the peak intensity of m-formate and b-formate as a function of time for both MgOZrO₂ and Cu/MgOZrO₂ under H₂ flow following exposure to CO₂ (Figs. 5b and c, and Supplementary Figs. 37b and 38b). Consumption or desorption of both b-formate and m-formate was more rapid on Cu/MgOZrO₂ than on MgOZrO₂.



Supplementary Figure 38. Time-dependent in situ DRIFT spectra of MgOZrO₂ under (a) CO₂ and (b and c) under H₂ flow at 250 °C and 1 bar.



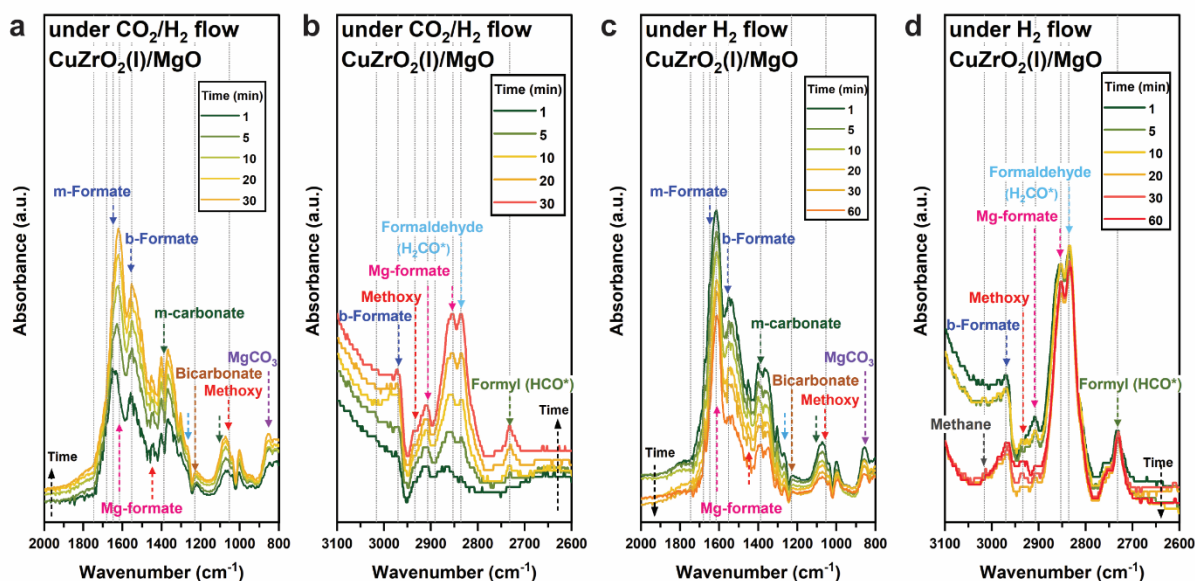
Supplementary Figure 39. Time-dependent in situ DRIFT spectra of Cu/MgOZrO₂ under (a and b) CO₂/H₂ flow and (c and d) under H₂ flow at 250 °C and 1 bar.



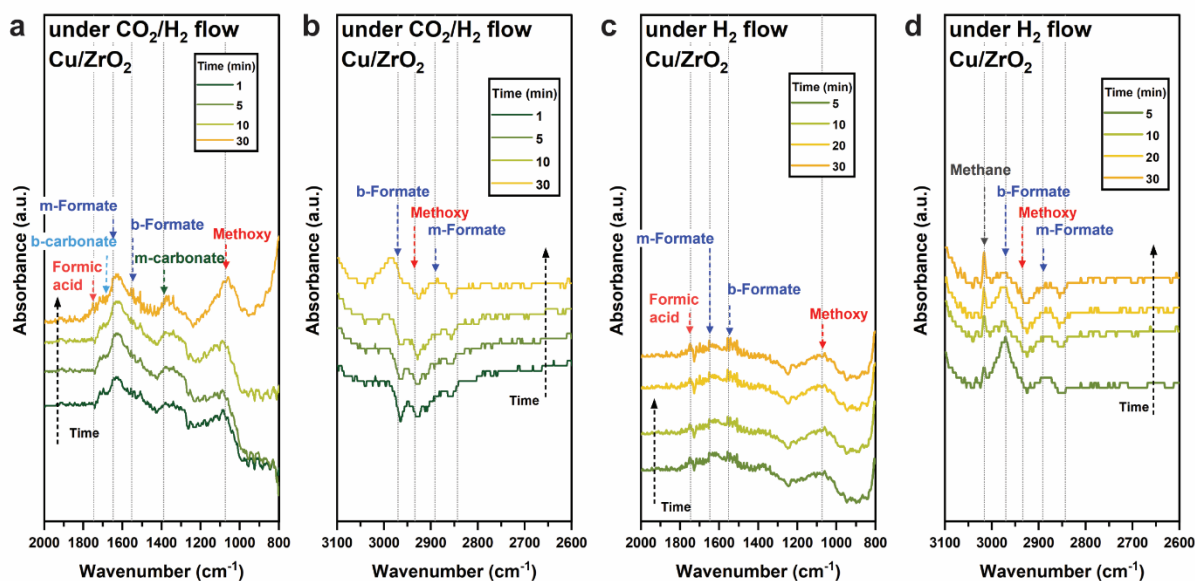
Supplementary Figure 40. Time-dependent in situ DRIFT spectra of Cu/MgO under (a and b) CO₂/H₂ flow and (c and d) under H₂ flow at 250 °C and 1 bar.

Supplementary Note 14: In contrast to Cu/MgOZrO₂, Mg-formate hardly desorbed or even accumulated on Cu/MgO under H₂ flow (see peaks resulting from Mg-formate at 1603 or 2855 cm⁻¹, [Supplementary Figs. 40c and d](#)). The absence of m-formate in Cu/MgO, which is an essential species to hydrogenate b-formate to the next intermediate (dioxymethylene), indicates that Cu/ZrO_x clusters more efficiently stabilized m-formate than Cu/MgO. Of note, b-formate relatively rapidly disappeared while the methoxy and formaldehyde groups accumulated. Therefore, the formyl was likely hydrogenated to formaldehyde and the methoxy via the reverse water gas shift followed by the CO hydrogenation pathway in this H₂-rich environment.¹⁵ The accumulation of formaldehyde on the surface of Cu/MgO can be explained by the existence of low-coordinated sites on the MgO800 support where the formaldehyde can strongly bind via its carbonyl moiety.¹⁶ Moreover, the low selectivity toward methanol (*i.e.*, high CO selectivity) when using Cu/MgO ([Fig. 3a](#)) and the absence of methoxy groups and formaldehyde on the surface of Cu/MgO under CO₂/H₂ flow ([Fig. 6a](#)) could also be explained

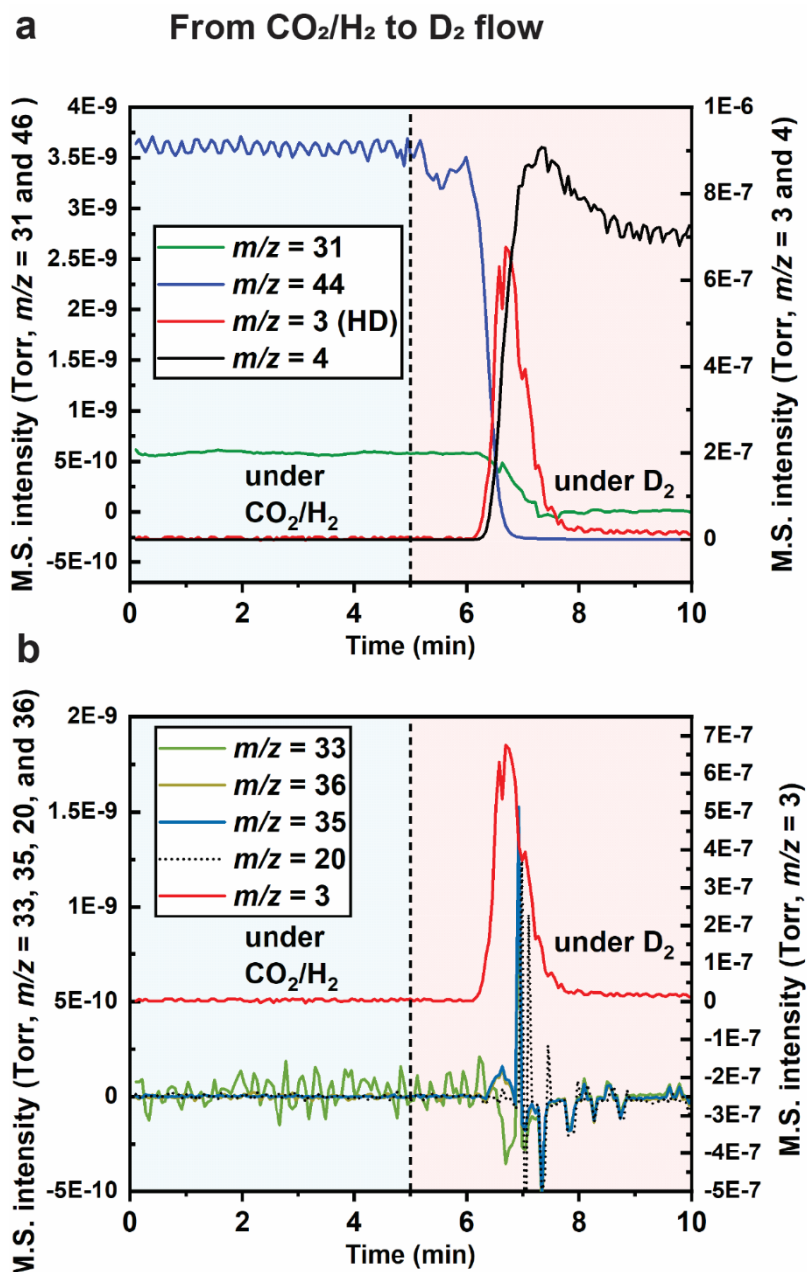
by the rapid dissociation of formyl to CO^* and H^* without further hydrogenation on a Cu-based catalyst in a hydrogen poor environment.¹⁵



Supplementary Figure S41. Time-dependent in situ DRIFT spectra of $\text{CuZrO}_2(\text{I})/\text{MgO}$ under (a and b) CO_2/H_2 flow and (c and d) under H_2 flow at 250 °C and 1 bar.



Supplementary Figure 42. Time-dependent in situ DRIFT spectra of Cu/ZrO_2 under (a and b) CO_2/H_2 flow and (c and d) under H_2 flow at 250 °C and 1 bar.

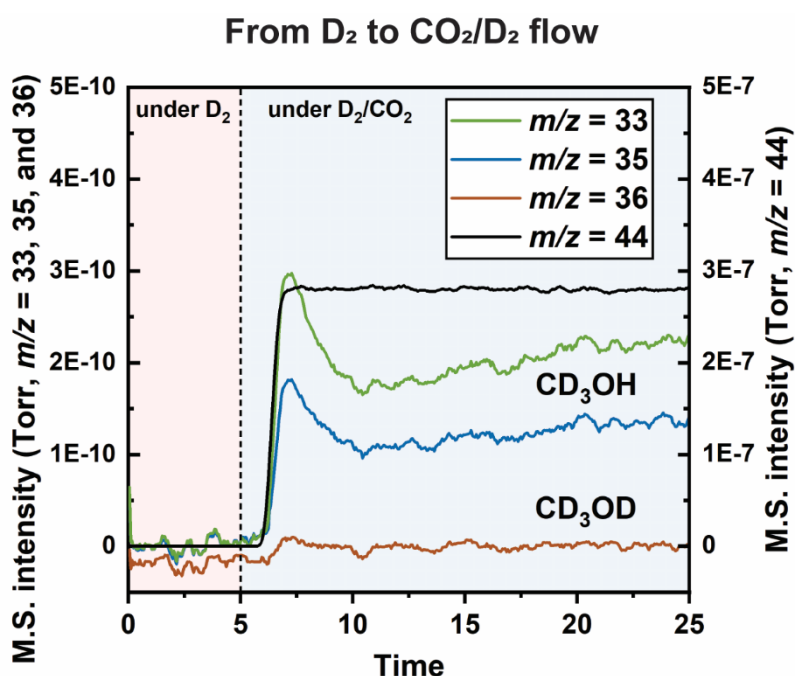


Supplementary Figure 43. Effluent gas profiles detected by the mass spectrometer from Cu/MgZrO₂ at 250 °C and 1 bar before and after switching the feed gas from the CO₂/H₂ mixture to D₂. [Figure 43a and b](#) were obtained with an identical experiment but with different m/z being detected.

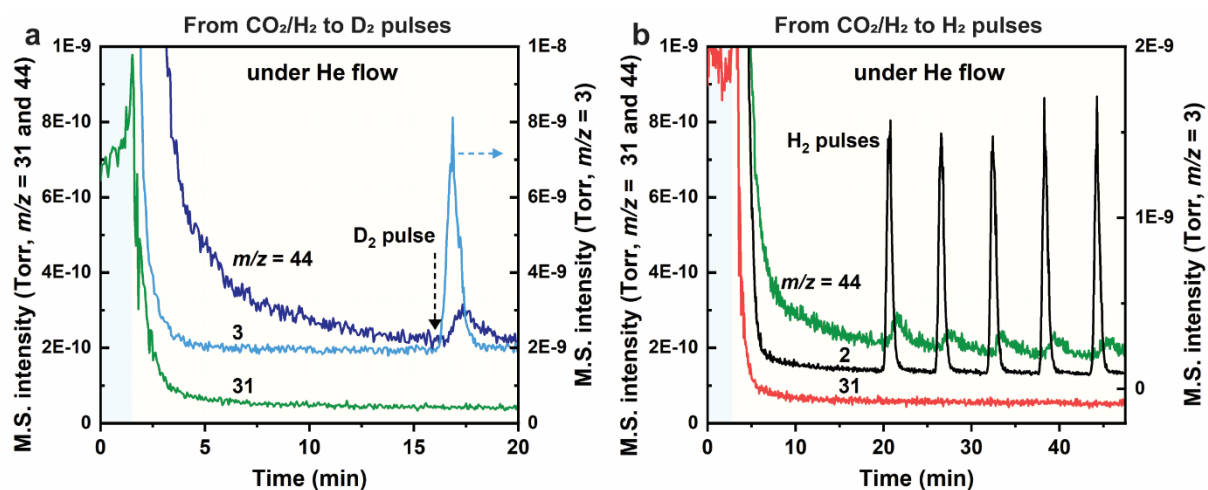
Supplementary Note 15: We further conducted experiments using deuterium (D₂) to identify the reacted intermediates after the shut-off of CO₂. When a D₂ flow followed the CO₂/H₂ flow instead of H₂, a large peak of $m/z = 3$ appeared due to H/D exchange with adsorbed hydrogen, and methanol production continued for around 3 min but deuterated methanol with an $m/z = 33, 35$, or 36 was hardly observed ([Supplementary Fig. 43](#)). The sharp evolution of $m/z = 35$ and 36 in [Supplementary Fig. 43b](#) could not be confidently attributed to the production of deuterated methanol due to the fluctuation resulting from the abrupt huge production of $m/z = 3$, as observed from the profile of $m/z = 20$, which is not related to any reactants or products. However, when we switched from this D₂ back to the CO₂/D₂ flow, the production of deuterated methanol appeared clearly ([Supplementary Fig. 44](#)). To observe desorbed or decomposed gases while introducing D₂ or H₂, D₂ and H₂ pulse experiments were conducted ([Supplementary Fig.](#)

45). After CO₂/H₂ flow (Supplementary Fig. 45a), Cu/MgOZrO₂ was purged with He and then 16 μ mol of a D₂ or H₂ pulse was injected. During the D₂ pulse, no deuterated methanol was detected, whereas CO₂ and HD were observed, which means that either the adsorbed species were decomposed or CO₂ was desorbed as an effect of the D₂ pulse. However, the m-formate was not hydrogenated to deuterated methanol. The H₂ pulse experiment also showed the same phenomena in Supplementary Fig. 45b.

The lack of production of deuterated methanol under D₂ flow after the shut-off of CO₂ can be explained by the mechanism of hydrogenation of methoxy to methanol. The source of hydrogen in producing methanol by hydrogenation of H₂COO* (dioxymethylene) and CH₃O* (methoxy) was recently proposed to be the proton of OH*, not the adsorbed hydrogen on the Cu surface.^{12,17} For the formation of OH*, the presence of CO₂ or H₂O is required, thereby methanol cannot be produced under pure H₂ flow. For this reason, the m-formate under CO₂/H₂ flow could be not converted to deuterated methanol and only methanol was produced from the reaction between CH₃O*, which was already generated under CO₂/H₂ flow, and the (already present) surface hydroxyl group. Since the formation of deuterioxyl on the surface of ZrO₂ is inhibited by the presence of adsorbed formates species, it is likely difficult to observe the deuterated methanol resulting from the reaction between deuterioxyl species (formed by an H/D exchange of surface hydroxy groups) and the adsorbed methoxy.¹⁸ The detection of a larger intensity of CD₃OH ($m/z = 33$ and 35) than CD₃OD ($m/z = 36$) under D₂/CO₂ flow followed by H₂/CO₂ and D₂ flow revealed the important role of the OH* as a source of hydrogen in producing methanol (Supplementary Fig. 44). This result suggests that surface OH groups on Cu/MgOZrO₂ were not completely consumed under D₂ flow (Supplementary Fig. 4a) and could still participate in the production of CD₃OH under the subsequent D₂/CO₂ flow. We conclude that the hydrogenation of m-formate to the final product, *i.e.* methanol, was only possible when the surface OH groups were available on an adjacent surface.



Supplementary Figure 44. Effluent gas profiles detected by mass spectrometer from Cu/MgZrO₂ at 250 °C and 1 bar after switching D₂ flow to D₂/CO₂ flow, after the experiment shown in Supplementary Figure 43.



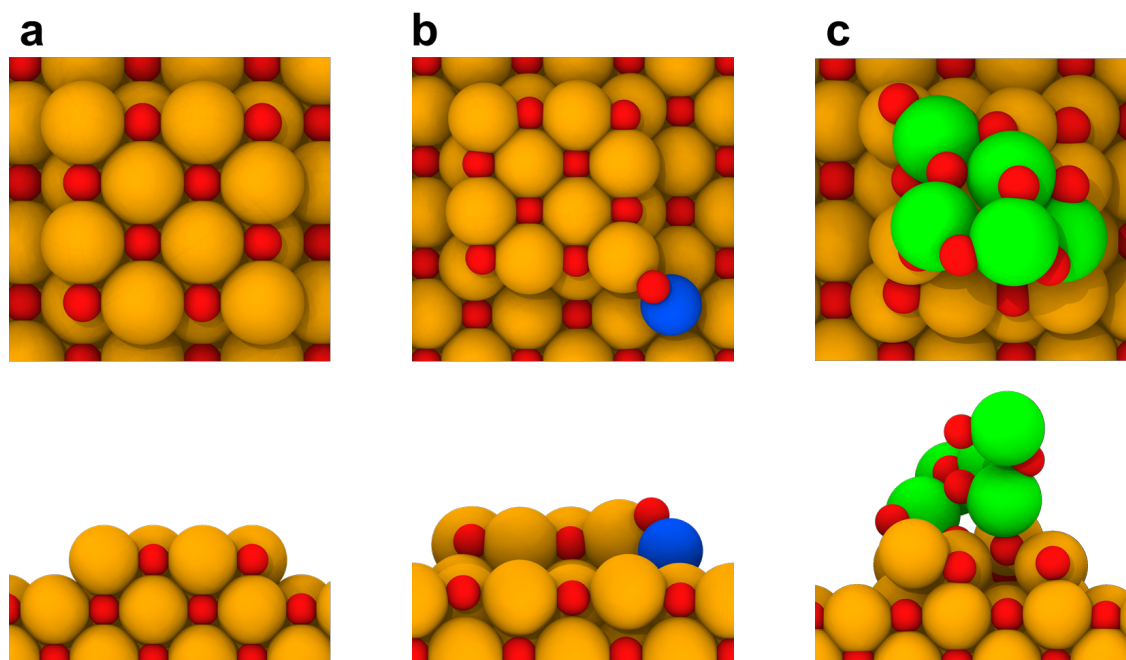
Supplementary Figure 45. Effluent gas profiles detected by mass spectrometer from Cu/MgZrO₂ at 250 °C and 1 bar during the (a) D₂ or (b) H₂ pulse experiments following the experiment under CO₂/H₂ flow.

Supplementary Discussion 2: Model systems for *ab initio* calculations and characteristic of the catalysts

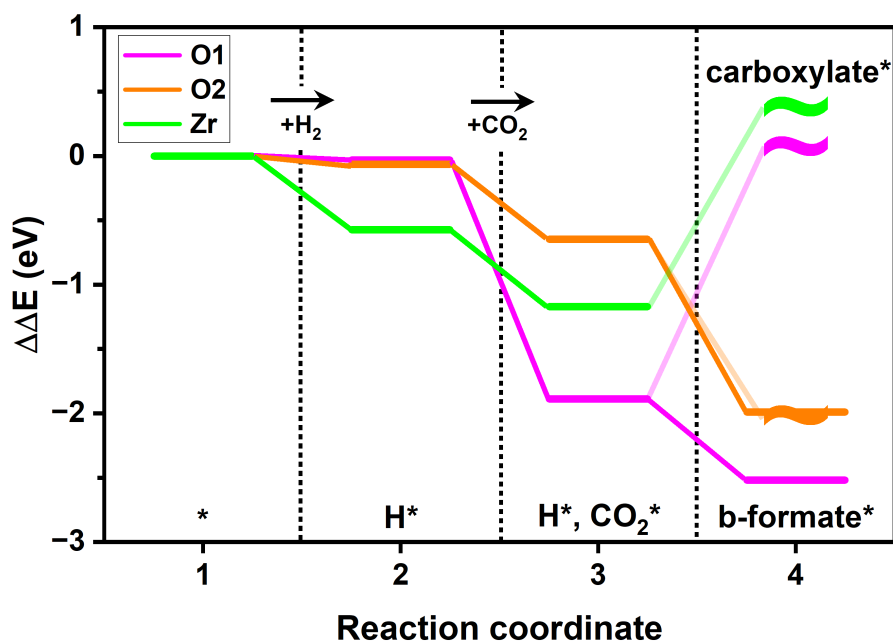
Model systems for *ab initio* computations^{19–22} were constructed in accordance with the experimentally identified features. The three-layer MgO support was prepared with an island on the (001) facet, containing the active sites of Mg_{3C} and O_{3C} (Supplementary Fig. 46a). To capture a simplified Cu-oxide interface, Cu/MgO was modeled by adding a single Cu atom bridged by O atom and Mg_{3C} site. MgOZrO₂ was modeled by adding a Zr₅O₉ cluster adsorbed on the Mg_{3C} site and its immediate surroundings. Zr₅O₉ was chosen instead of Zr₅O₁₀ due to the shared oxygen atoms at the interface of MgO and ZrO_x. All ionic positions were fully relaxed via *ab initio* computations for each added species on MgO support. The simplified model system for reduced Cu/MgOZrO₂ was constructed by first removing an oxygen atom in the adsorbed Zr₅O₉ cluster to reflect the reduction process and adding a Cu atom near the oxygen vacancy (Supplementary Fig. 46b-c). Since the computational cost to simulate a Cu nanoparticle evolving in reaction conditions far exceeds the feasible of our DFT calculations, we modeled a single Cu atom rather than a Cu nanoparticle to capture the interface between the Cu and the ZrO_{2-x} cluster. We believe the chemical nature of the Cu atom in our model system would be highly similar to that of the interfacial Cu atom in a Cu nanoparticle interfaced with a ZrO_{2-x} cluster, as we expect the catalytic reaction to take place mostly at the partially bonded Cu atom-ZrO_{2-x} interface. When creating an oxygen vacancy and adding a Cu atom in MgOZrO₂, a total of 7 distinct configurations were sampled and fully relaxed in terms of ionic positions (Supplementary Fig. 50 and 51). The relaxed configuration with the lowest energy is shown in Supplementary Fig. 51a. The added Cu atom in modeled Cu/MgOZrO₂ has the nearest Zr distanced at 2.61 Å, followed by the second nearest Zr at 3.44 Å (Supplementary Fig. 50c and 51b). All 7 configurations exhibit at least one (and up to three) Zr neighboring Cu within 2.85 Å, the Zr-Cu bond length in Zr₂Cu alloy. This result agrees with the interpretation from WT-EXAFS in Fig. 4f showing some Cu-Zr interaction. Some of the model systems contain closely bonded oxygen near the Cu atom (Supplementary Fig. 51c), yet the majority of the Cu-O bonds are joined by Zr atom with the distances between 2.98 Å and 3.36 Å (Supplementary Fig. 51d). Bader charge analyses^{23,24} show similar Bader charges for Zr and Cu atoms among the 7 distinct configurations, with Zr atoms reduced compared to the bulk ZrO₂ counterpart in m-ZrO₂ and Cu atoms exhibiting gained electron charges (-0.38 ~ -0.61) than Cu metal (Supplementary Fig. 52).

To model the CO₂ hydrogenation reaction mechanism on Cu/MgOZrO₂, we needed to identify the potential co-adsorption sites for H and CO₂. Since the number of configurations for the co-adsorption was very high, we assumed that the adsorption of H atoms precedes the CO₂ hydrogenation reaction. The hydrogen adsorption sites (19 sites) on the model system (Supplementary Fig. 50a) are first screened and identified with universal neural network potentials²⁵ and the adsorption energies were computed with density functional theory calculations (Supplementary Fig. 53a). The resulting adsorbed H atom was preferentially adsorbed on the surface Cu and Zr atoms rather than the O atoms with respective adsorption energies of -0.33 eV, -0.57 eV and -0.03 ~ -0.07 eV on the modeled Cu/MgOZrO₂. We selected 7 adsorption sites (Supplementary Fig. 53b) and compared the adsorption energy calculated by DFT and PFP potential to validate the screening capabilities of the PFP potential. The PFP potential does not predict the exact strength of H adsorption, but the trends are the same confirming that it's a useful tool to screen feasible H adsorption sites. The metal-adsorbed and oxygen-adsorbed H atoms on the catalyst lead to the formation of a hydride and a hydroxide, respectively (Supplementary Fig. 53b). CO₂ molecules are then adsorbed near the adsorbed H atoms and allowed to full relax in terms of ionic positions to identify the atomic configurations of adsorbed CO₂. Importantly, we used the PFP potential only to screen feasible H adsorption

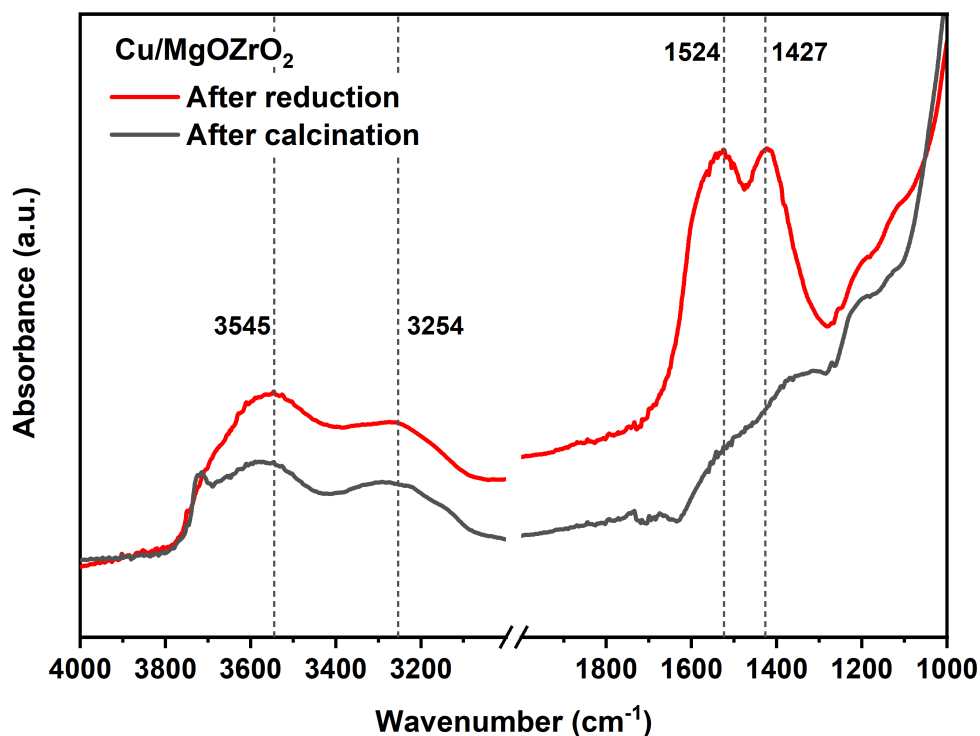
sites on the Cu/MgOZrO₂ catalyst, while all reaction energies are computed using DFT calculations.



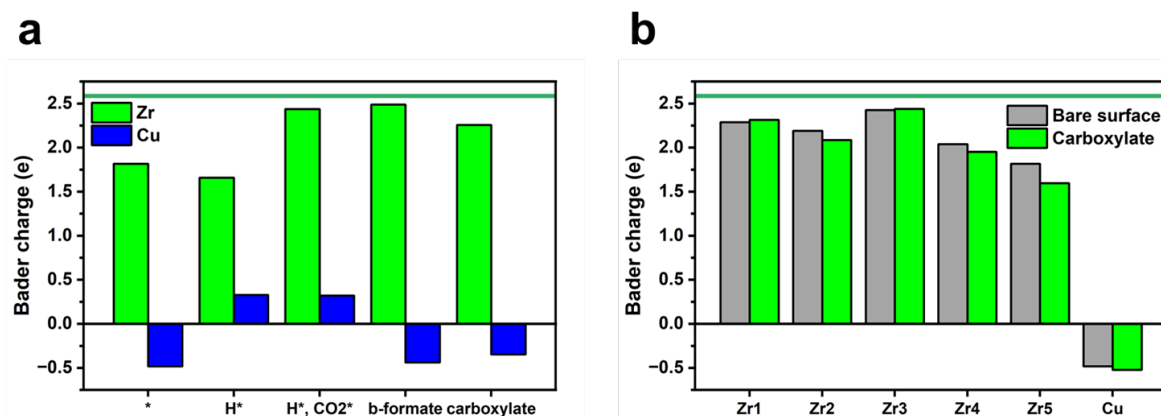
Supplementary Figure 46. Model systems of (a) MgO, (b) Cu/MgO and (c) MgOZrO₂ catalysts, respectively. The orange, blue, green and red spheres represent Mg, Cu, Zr and O atoms, respectively.



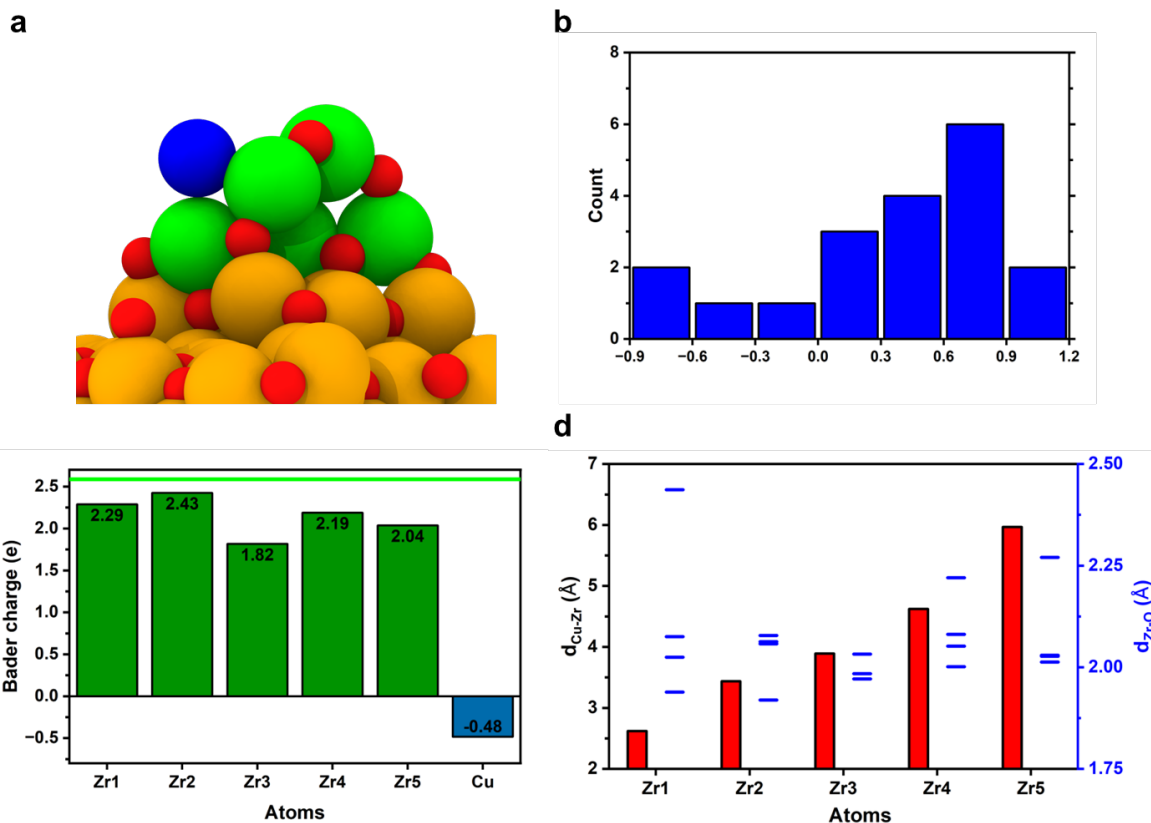
Supplementary Figure 47. Reaction mechanisms of CO₂ hydrogenation initiated by H adsorptions on either O1, O2 or Zr atoms as shown in [Supplementary Figure 53](#).



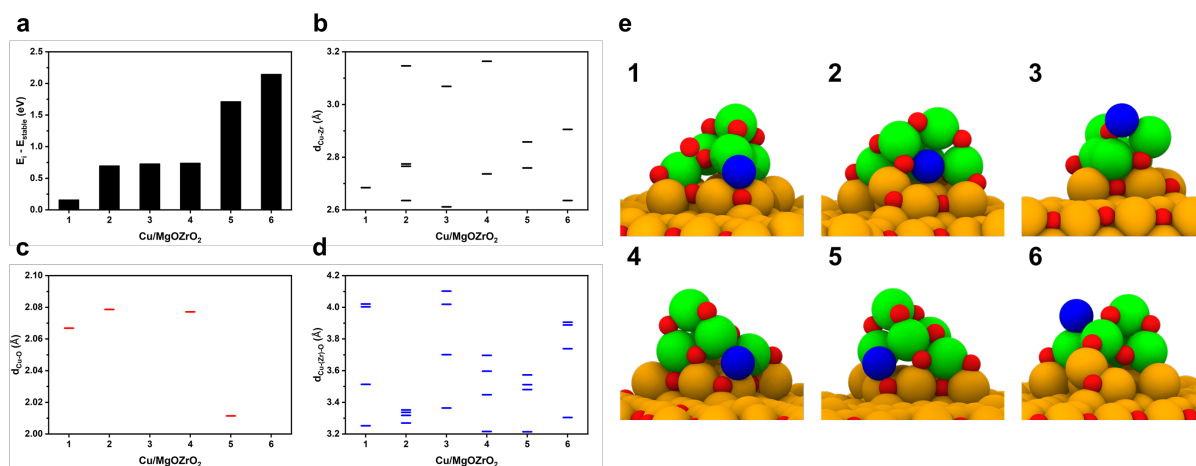
Supplementary Figure 48. DRIFT spectra of Cu/MgZrO₂ obtained during in situ calcination under He flow and reduction under 10%H₂/Ar flow. This result supports the formation of zirconium hydride after adsorption of H₂ (1524 and 1427 cm⁻¹)²⁶ and multi-coordinated OH groups (3200 ~ 3600 cm⁻¹)³.



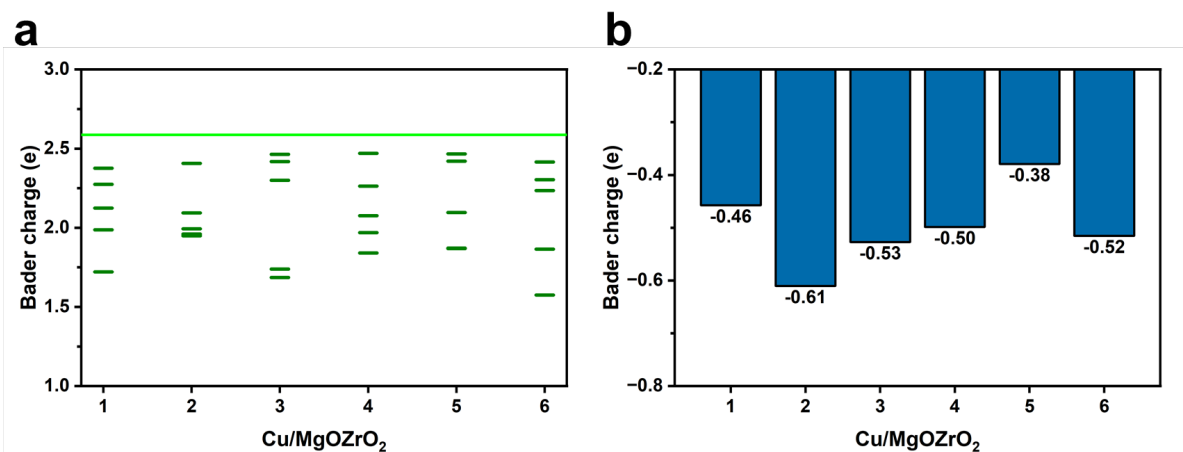
Supplementary Figure 49. Bader charges of (a) Zr and Cu atoms as a function of reaction coordinates when H adsorbed on the Cu atom (energies depicted in Fig. 7a) and (b) Zr and Cu atoms for either a bare surface or carboxylate adsorbed surface (the latter corresponds to the green wavy line in Supplementary Fig. 47).



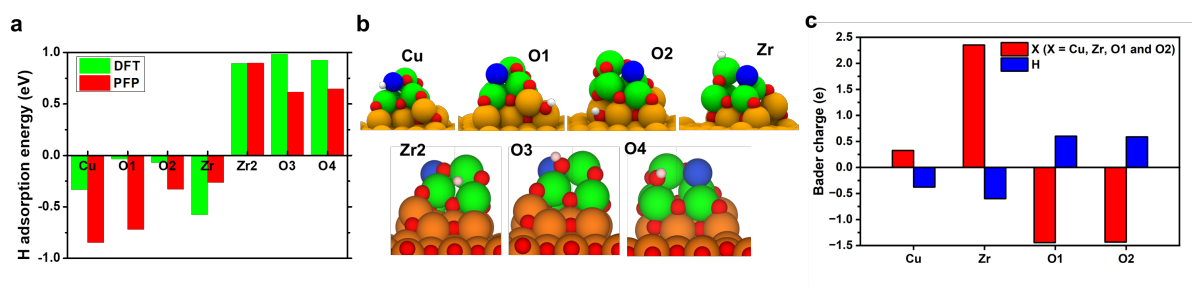
Supplementary Figure 50. (a) The model system of Cu/MgOZrO₂ catalyst viewed from the side. The orange, red, green and blue color indicate Mg, O, Zr and Cu elements, respectively. (b) Adsorption energy of H atom on Cu/MgOZrO₂ model system by PFP potential. (c) Bader charges of Cu and Zr atoms in (a). (d) The Cu-Zr and Zr-O neighbor distances for each Zr atom in the model system.



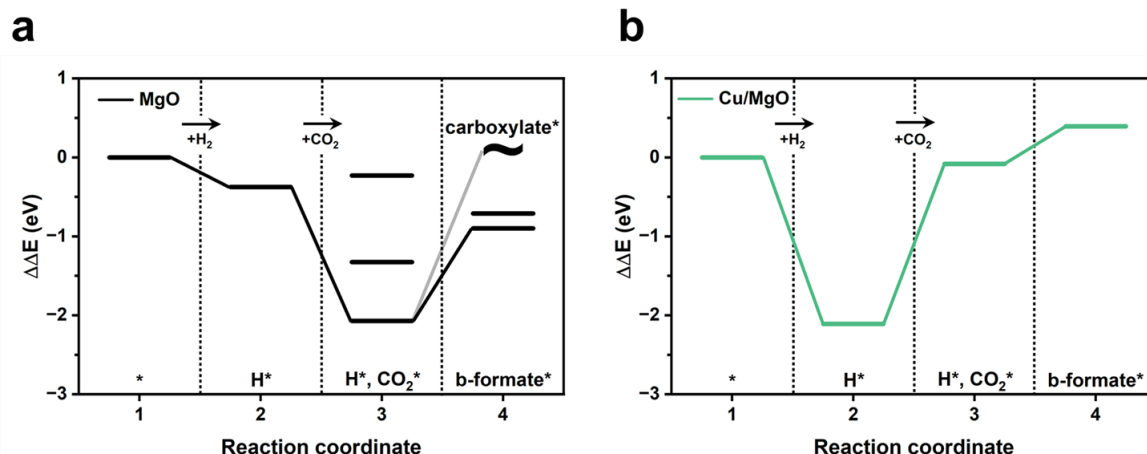
Supplementary Figure 51. (a) The energy difference with respect to the lowest energy model system in terms of the computed energy. The (b) Cu-Zr, (c) Cu-O and (d) Cu-(Zr)-O bond lengths in the computed metastable systems in (e). (e) The 6 metastable model systems of Cu/MgOZrO₂ depending on the location of the added Cu atom, with respect to the model system shown in [Supplementary Fig. 50a](#). The orange, blue green and red represent Mg, Cu, Zr and O elements, respectively.



Supplementary Figure 52. Bader charges of (a) Zr and (b) Cu atoms in the Cu/MgOZrO₂ metastable model systems in [Supplementary Fig. 51\(e\)](#). The light green line indicates the computed Bader charge of Zr in m-ZrO₂.

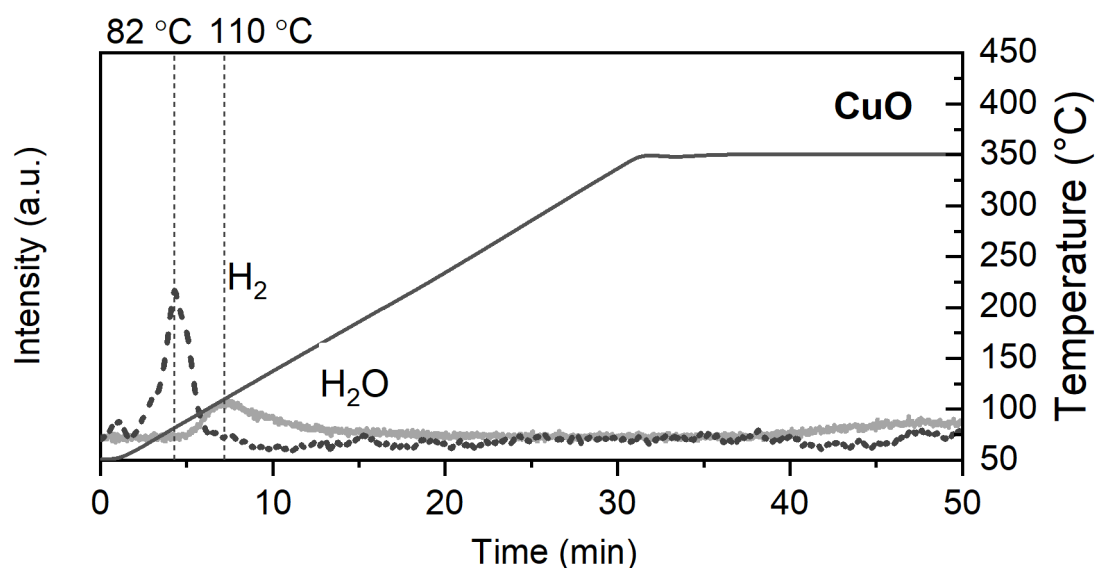


Supplementary Figure 53. (a) Adsorption energy of H atoms calculated by DFT and PFP potential and (b) the computed configuration and on the modeled Cu/MgOZrO₂ catalyst. The orange, red, green, blue and pink color represent Mg, O, Zr, Cu and H elements, respectively. (b) The computed Bader charges of H and the adsorbent atom depending on the adsorption sites.



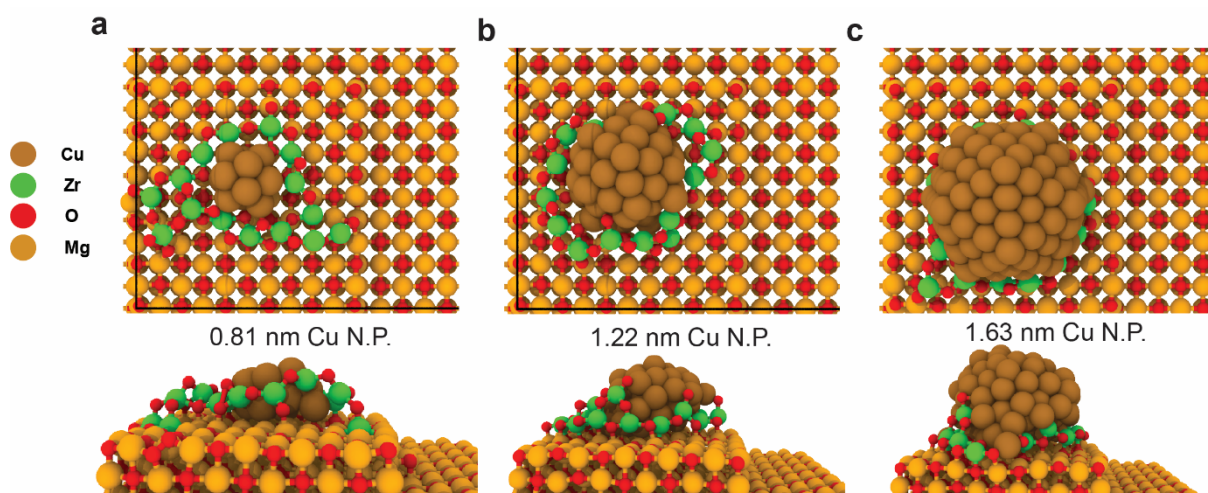
Supplementary Figure 54. Reaction mechanisms on (a) MgO and (b) Cu/MgO catalysts, corresponding to [Supplementary Figs. 46 and b](#), respectively. The b-formate and carboxylate states are distinguished by straight and wavy lines, respectively.

Supplementary Note 16: The reaction mechanisms on MgO and Cu/MgO were investigated. The H adsorption occurs on the O and Cu atoms of MgO and Cu/MgO catalysts, respectively. The CO₂ strongly adsorbed on the sites adjacent to the H atom on the MgO catalyst, which is too strongly stabilized to proceed the next step, which is a b-formate intermediate (shown in [Supplementary Fig. 54a](#)). The co-adsorption of H and CO₂ molecules on Cu/MgO is unstable whereas the carboxylate is stable compared to b-formate ([Figure 7a](#) and [Supplementary Fig. 54b](#)).



Supplementary Figure 55. H₂-TPA profile of the reduced CuO (abcr GmbH; 99.995%-Cu) at 350 °C; Dotted line: Signal of $m/z=18$ corresponding to H₂O; Dashed line: TCD signal. H₂ consumption was estimated from the peak in TCD signal is 9.8 $\mu\text{mol/g}$ CuO. This value only amounts to $7.8\text{E-}05$ of the total Cu moles in CuO.

Supplementary Note 17: To verify that the consumption of H₂ at 92 °C and the evolution of H₂O at 250 °C observed during H₂-TPA of the reduced Cu/MgOZrO₂ occurred exceptionally in the Cu/MgZrO₂ catalyst, normal CuO, Cu/ZrO₂ catalyst, and MgOZrO₂ having only ZrO₂ clusters were subjected to the same experiment. MgOZrO₂ did not exhibit H₂ consumption. On the other hand, normal CuO after reduction at 350 °C consumed H₂ and generated H₂O but its H₂ consumption was 9.8 $\mu\text{mol/g}$ CuO, which only amounts to $7.8\text{E-}05$ of total Cu moles in CuO. We speculated that H₂ consumption accompanied with H₂O at the low temperature resulted from the migrated oxygen from the subsurface.¹⁰



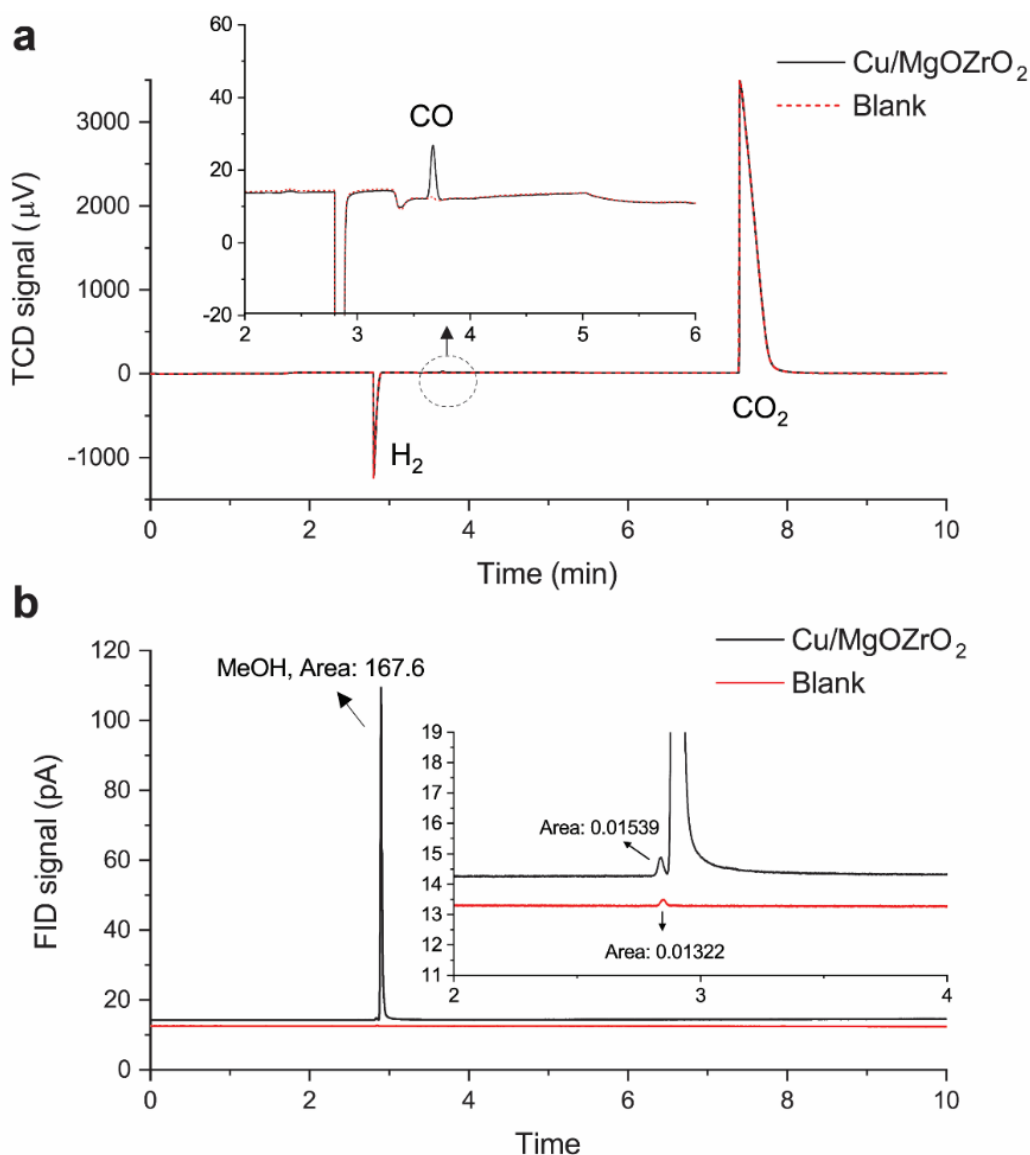
Supplementary Figure 56. Simulated structure of Cu/MgOZrO₂ with different sizes of Cu nanoparticles (N.P.) surrounded by ZrO_x clusters. a, 0.81 nm Cu N.P. b, 1.22 nm Cu N.P. c, 1.63 nm Cu N.P. The percentages of Cu atoms at the Cu-Zr interface to the total Cu atoms in the nanoparticle were 27% (15/55), 10% (15/147), and 5% (15/309), respectively.

Supplementary Discussion 3: Possible errors in selectivity resulting from unclosed carbon balance in CO₂ hydrogenation tests.

Since the conversion of Cu/MgOZrO₂ catalyst is kept low (<2%) to remain far from equilibrium, even small deviations in carbon balances (<0.5%) could in theory lead to errors. Here, we discuss how we have avoided these pitfalls. The STY measurement is normalized by the residence time and thus does not actually depend on conversion (provided all conversions are sufficiently small to be far from equilibrium, which is the case here). To illustrate the reproducibility of the method, we have repeated several measurements, which were highly reproducible. The error range of STY ($\text{g}_{\text{MeOH}} \text{g}_{\text{Metal}}^{-1} \text{h}^{-1}$) of Cu/MgOZrO₂ estimated by four GC measurement was ± 0.08 in a single run. We also tested reactivity of Cu/MgOZrO₂ from three different batches and its error range was ± 0.7 . These error ranges are substantially smaller than the difference in activity with other control catalysts. For example, STY of Cu/MgOZrO₂ was $16.3 (\pm 0.7) \text{ g}_{\text{MeOH}} \text{g}_{\text{Metal}}^{-1} \text{h}^{-1}$ whereas the STY of the commercial Cu/ZnO/Al₂O₃ was $5.16 (\pm 0.04)$.

Selectivity calculations can be more sensitive to conversion. However, we have systematically used the sum of products instead of the conversion to calculate selectivity. This provides excellent accuracy provided we are not missing a product which could be revealed by a mass balance below 100%. Nevertheless, the 99.5% mass balance closure is likely below 100% due to GC error rather than a missed product, which is strongly supported by the appearance of the chromatogram below ([Supplementary Figure 57](#)). These chromatograms show no products other than CO and methanol, suggesting that the missing carbon balance probably resulted from the fluctuation of CO₂ in the MFC or in the GC sampling loop, rather than from undetected products. In [Supplementary Table 8](#), the standard deviation of the CO₂ peak area during the blank test was around 0.3% of the mean value, which largely explains the mass balance closure issue.

Nevertheless, to be transparent, we are now reporting the actual deviations in mass balance closure and the maximum selectivity error that could result from this entire deviation being due to an unknown product, which we judge to be highly unlikely ([Supplementary Tables 9 and 10](#) for Cu/MgOZrO₂ and Cu₂L/MgOZrO₂, respectively). As is revealed, this maximum error is never sufficient to change our conclusions.



Supplementary Figure 57. Chromatograms of (a) TCD signal and (b) FID signal obtained during CO₂ hydrogenation of Cu/MgOZrO₂ and blank test. H₂, CO, and CO₂ were detected from the TCD signal. Methanol and a small peak were detected from the FID signal during the reaction. A small peak preceding the methanol peak was also observed during the blank, and its area was negligible compared to that of the methanol peak. Therefore, it was not considered a product of the reaction.

Supplementary Tables

Supplementary Table 1. ICP-MS results and BET specific surface area of the as-prepared catalysts.

Method/Support	Catalysts	Composition (wt.%)					BET specific surface area (m ² /g) ^a
		Mg	Zr	Cu	In	Zn	
MgO500	MgO500	-	-	-	-	-	96.8
MgO800	MgO800	-	-	-	-	-	67.0
ZrO ₂ -C	ZrO ₂ -C-500	-	-	-	-	-	5.6
ALD/MgO800	MgOZrO ₂	62.31	5.37	-	-	-	49.6
ALD/MgO800	Cu/MgOZrO ₂ -3L	56.2	2.88	0.709	-	-	-
ALD/MgO800	Cu/MgOZrO ₂	60.60	4.94	0.548	-	-	35.7
ALD/MgO800	2LCu/MgOZrO ₂	57.19	4.50	1.080	-	-	-
ALD/MgO800	Zn/MgOZrO ₂	59.10	5.02	-	-	1.542	43.9
ALD/MgO800	Cu/MgO	58.93	-	0.517	-	-	40.1
ALD/ZrO ₂ -C	Cu/ZrO ₂	-	73.86	0.185	-	-	3.6
IWI/MgO800	Cu(I)/MgOZrO ₂	60.51	5.15	1.113	-	-	49.2
IWI/MgO800	CuZrO ₂ (I)/MgO	55.27	4.94	1.340	-	-	36.1
IWI/MgO800	Zn(I)/MgOZrO ₂	63.52	5.77	-	-	1.227	16.1
IWI/ZrO ₂ -C	Cu(I)/ZrO ₂	-	51.30	0.109	-	-	-
ALD/MgO500	MgO500ZrO ₂	36.64	10.728	-	-	-	97.4
ALD/MgO500	Cu/MgO500ZrO ₂	36.93	10.35	1.02	-	-	-
ALD/MgO500	Zn/MgO500ZrO ₂	47.29	14.59	-	-	3.239	-
Hifuel	Cu/ZnO/Al ₂ O ₃	-	-	42.50	-	25.58	-

^aObtained from N₂ adsorption/desorption isotherm measured at 77K

Supplementary Table 2. Quantitative analysis of surface elements obtained from XPS spectra.

Catalysts	O 1s					
	O _{OH}		O _D		O _L	
	Position	Area	Position	Area	Position	Area
	(eV)	(%)	(eV)	(%)	(eV)	(%)
MgO800	532.71	24.5	531.22	32.0	530.34	42.5
MgOZrO ₂	533.02	10.1	531.25	51.2	530.47	38.7
Cu/MgO	532.80	22.7	531.46	34.8	530.40	42.5
Cu/MgOZrO ₂	532.35	21.6	531.64	33.6	530.27	44.8
Cu/ZrO ₂	533.13	28.4	532.21	25.1	530.53	46.5

Catalysts	Zr 3d	
	Zr ⁴⁺	Zr ^{q+} (q<4)
	(%)	(%)
MgOZrO ₂	33.6	66.4
Cu/MgOZrO ₂	56.0	44.0
Cu/ZrO ₂	62.8	41.2

Supplementary Table 3. Summary of the space time methanol yield (STY) and the selectivity of as-prepared catalysts.

Method/Support	Catalysts	STY (g _{MeOH} g _{metal} ⁻¹ h ⁻¹)	Selectivity (%)	TOF ^c
ALD/MgO800	MgOZrO ₂	0	0	-
ALD/MgO800	Cu/MgOZrO ₂ -3L	2.68	54.9	-
ALD/MgO800	Cu/MgOZrO ₂	16.3 (±0.7)	76.7 (±0.9)	250 (±12.6)
ALD/MgO800	2LCu/MgOZrO ₂	12.95	76.8	-
ALD/MgO800	Zn/MgOZrO ₂	0.33	100	-
ALD/MgO800	Cu/MgO	2.52	24.1	-
ALD/ZrO ₂ -C	Cu/ZrO ₂	3.97	34.9	-
IWI/MgO800	Cu(I)/MgOZrO ₂	0.39	38.9	-
IWI/MgO800	CuZrO ₂ (I)/MgO	0.14	9.6	-
IWI/MgO800	Zn(I)/MgOZrO ₂	0.24	100	-
IWI/MgO800	In(I)/MgOZrO ₂	0	0	-
IWI/ZrO ₂ -C	Cu(I)/ZrO ₂	0	0	-
ALD/MgO500	MgO500ZrO ₂	0	0	-
ALD/MgO500	Cu/MgO500ZrO ₂	6.30	68.4	-
ALD/MgO500	Zn/MgO500ZrO ₂	0	0	-
Commercial				
methanol synthesis catalyst	Cu/ZnO/Al ₂ O ₃ ^a	5.16 (±0.04)	54.0 (±0.18)	101 (±0.8)
HiFUEL	Cu/ZnO/Al ₂ O ₃ ^b	4.28 (±0.07)	64.3(±0.1)	116 (±1.0)

^aMeasured at the high GHSV condition of 183,000 ml g_{cat}⁻¹ h⁻¹ where CO₂ conversion was lower than 5%

^bMeasured at the high GHSV condition of 209,790 ml g_{cat}⁻¹ h⁻¹ where CO₂ conversion was lower than 5%; This catalyst is optimized for the water gas shift (WGS) reaction.

^cAn error bar for Cu/MgOZrO₂ was obtained by repeating the activity test, batch-to-batch, three times. The error for the commercial catalysts was estimated using the standard deviation from four GC measurements.

Supplementary Table 4. Comparison of CO₂ hydrogenation catalysts for methanol production.

Catalyst	Synthesis method	Reaction temperature (°C) / pressure (bar)	Feed conditions	Metal loading (wt.%)	Methanol STY (g _{MeOH} g _{Metal} ⁻¹ h ⁻¹)	Methanol selectivity (%)	Ref.
Cu/MgOZrO ₂	Liquid-phase ALD	250/ 30	H ₂ :CO ₂ = 3:1	0.548	16.3 (±0.7)	76.7 (±0.9)	This study
		200/ 30			2.97	100	
		250/ 1			1.95	31.3	
Cu/Mo ₂ CT _x /SiO ₂ -6h	Surface organometallic chemistry	230/ 25	H ₂ :CO ₂ :N ₂ = 3:1:1	2.4	2.5	52	17
Cu-N ₄ SAC (C ₃ N ₄ -supported single Cu atom)	Thermal pyrolysis of melamine	150/ 32	H ₂ :CO ₂ :N ₂ = 72:24:4	12.1	0.13	95.5	27
Three-dimensional ordered microporous Cu/ZnO/ZrO ₂ ^a	Colloidal crystal template	220/ 30	H ₂ :CO ₂ = 3:1	33.56 ^a	0.89 ^a 1.73 ^a	80.4 ^a 91 ^a	28
Inverse ZrO ₂ /Cu ^b	Co-precipitation	220/ 30	H ₂ :CO ₂ = 3:1	72.1 (Cu) / 9.3 (Zr)	0.73 (Cu) / 5.61 (Zr)	70.3	29
Single-atom Cu/ZrO ₂ ^c	Co-precipitation	180/ 30	H ₂ :CO ₂ :Ar = 0.72:0.24:0.04	0.97	0.68 ^c	100	30

Cu-In-Zr-O mixed oxide	Co-precipitation	250/ 25	H ₂ :CO ₂ = 3:1	17.93	0.44	79.7	31
CZA/SiO ₂ -6	Commercial Cu/ZnO/Al ₂ O ₃ mixed with SiO ₂	210/ 34	H ₂ :CO ₂ = 5:1	3.6	0.13	66.1	32
CS25 ^d	Co-precipitation- deposition	280/ 50	H ₂ :CO ₂ :N ₂ = 72:24:4	21	1.82	35.8	33
CZ-8-350 ^e	Incipient wetness impregnation	230/ 10	H ₂ :CO ₂ :N ₂ = 3:1:1	8	0.56	72	7
Cu(45)/ZnO-CeO ₂ (y) ^f	Flame spray pyrolysis	250/ 30	H ₂ :CO ₂ :N ₂ = 3:1:1	39.8	1.54	50	34
Cu-Ga/SiO ₂	Surface organometallic chemistry	230/ 25	H ₂ :CO ₂ :N ₂ = 3:1:1	3.88	1.3	90	35
CuHT-230 ^g	Incipient wetness impregnation	230/ 20	H ₂ :CO ₂ :N ₂ = 71.3:23.7:5	9.4	0.89	70.5	36
Cu-Zn/SiO ₂	Surface organometallic chemistry	230/ 25	H ₂ :CO ₂ :N ₂ = 3:1:1	4.16	1.6	86	37
W-doped Cu/CeO ₂	Wet impregnation	250/ 35	H ₂ :CO ₂ :N ₂ = 69:23:8	10.9	3.62	87	38

Cu-ZnO/Pr ₂ O ₃ -NS ^h	Deposition-precipitation	260/ 30	H ₂ :CO ₂ :Ar = 24:72:4	17.5	2.26	75.4	39
Cu/AlCeO	Co-precipitation	260/ 30	H ₂ :CO ₂ :Ar = 9:3:1	61.2	0.623	22	40
LDH30Ga ⁱ	Aqueous miscible organic solvent treatment method	270/ 45	H ₂ :CO ₂ = 3:1	33.5	1.76	49	41
Cu/SiO ₂	Flame spray pyrolysis	190/ 30	H ₂ :CO ₂ = 3:1	17.8	0.17	79.3	42
Cu/TiO _{2-x} -500	Impregnation	300/ 40	H ₂ :CO ₂ = 3:1	5.91	1.57	43.3	43
Cu/ZnO _x @UiO-66	Co-precipitation with UiO-66 as structural template	260/ 40	H ₂ :CO ₂ :Ar = 24:72:4	48.61	0.45	52	44
Cu-0.5-300 ^j	In situ reconstruction of size confined Cu@UiO-66	260/ 45	H ₂ :CO ₂ = 3:1	12.4	6.42	78.8	45

^aCu loading was not specified, thus it was calculated from the TOF (0.0206 s⁻¹) and productivity (582.2 g_{MeOH} Kg_{cata}⁻¹ h⁻¹) obtained at low and high CO₂ conversions.

^bMetal loading for both Cu and Zr in inverse ZrO₂/Cu catalyst was calculated from the content of CuO and ZrO₂ provided in the literature and, due to this inverse configuration, methanol STY was also calculated based on either Cu or Zr.

^cMethanol STY in the unit of mmol_{MeOH} g_{Metal}⁻¹ h⁻¹ was calculated from CO₂ conversion, selectivity, molar flow rate of CO₂, and Cu loading via the equation presented in the literature and then converted into units of g_{MeOH} g_{Metal}⁻¹ h⁻¹ by multiplying with the molecular weight of methanol.

^dAmorphous 3D-structured Al-TUD-1 supported CuO-ZnO-ZrO₂

^eAmorphous ZrO₂-supported Cu catalyst

^fTernary Cu/ZnO-CeO₂

^gMg-Al Hydrotalcite-supported Cu catalyst

^hZnO-modified Cu-based catalyst over defect-rich Pr₂O₃ nanosheets

ⁱUltrathin (Cu)_{1-x}Ga_x-CO₃ layered double hydroxide (LDH)

^jCu@ZrO₂ framework catalyst that used in situ reconstruction

Supplementary Table 5. Parameters of the Cu *K*-edge EXAFS fits under CO₂ hydrogenation condition

Catalysts	Coordination number (CN)	<i>R</i> (Å)	σ (Å ²)	ΔE_0
Cu/MgOZrO ₂	7.06(11)	2.47(1)	0.0152(7)	−0.2(1.9)
Cu/ZrO ₂	7.18(8)	2.53(2)	0.013(1)	4.6(2.8)

Supplementary Note 18: To reduce the correlation between the coordination number and the Debye-Waller parameter, the correlation curves were plotted and the values were chosen at the intersection of the curves obtained for three different *k*-weighting ([Supplementary Figs. 34c and d](#)). We fitted the EXAFS spectra in the *k*-range of 3.5–10.5 Å^{−1} and the *R*-range of 1.0–3.0 Å. To approximately estimate the coordination number of the Cu-Cu scattering path, we slightly increased the lower boundary to reduce the influence of oxygen and reduced the upper boundary to cut the high-*k* part that contains the signal from Zr. The approximate estimation of average coordination number of Cu resulted in 7.06, which can be obtained from at least around 1 nm of Cu nanoparticle with an FCC structure.

Supplementary Table 6. Summary of wavenumbers and vibrational modes used for assigning the adsorbed surface species in in situ DRIFTS

Surface species	Assignment	Wavenumber (nm ⁻¹)	Cu/MgOZr ₂	In this study	
		Literature		Cu/MgO	CuZrO ₂ (I)/MgO
Monodentate formate (m-formate)	$\nu(\text{CO})$	1651 (Cu111) ¹²	1647	1647	N/D ^e
	$\nu(\text{CH})$	2893 (Cu/ZnO/SiO ₂) ⁴⁶	2891	2891	N/D
Bidentate formate on ZrO ₂ or Cu (b-formate)	$\nu_{\text{as}}(\text{OCO})$	1543 (ZrO ₂ Cu) ²⁹ , 1553 (Cu/SiO ₂) ⁴⁷ 1543 (b-formate on Cu in Cu/ZrO ₂ /SiO ₂) ⁴⁸	1553	1543	N/D
	$\delta(\text{CH})+$ $\nu_{\text{as}}(\text{OCO})$	2970 (Inverse ZrO ₂ Cu) ²⁹ 2970 (b-formate on ZrO ₂ in Cu/ZrO ₂ /SiO ₂) ⁴⁸	2970	2965	N/D
	$\nu_{\text{as}}(\text{CH})$	2907 (Mg formate) ⁴⁹	2907	2907	2907
Formates on Mg (Mg-formate)	$\nu_{\text{as}}(\text{CH})$	2839 (bridge formate on MgO) ¹⁴ 2862 (bidentate formate on Cu/MgO) ⁵⁰ 1603 (Mg formate) ⁴⁹	2866	2855	2855
	$\nu_{\text{as}}(\text{OCO})^a$	1626 (bidentate formate on Cu/MgO) ⁵⁰ 1595 (MgO) ⁵¹ 1606 (MgO(111)) ⁵²	1591	1603	1615
	$\nu_{\text{as}}(\text{CH}_3)$	2930 (Cu/SiO ₂) ⁵³ , 2934 (MgO(111)) ⁵²	2934	2933	2934
Methoxy	$\nu_{\text{s}}(\text{CH}_3)$	2815 (Cu/SiO ₂) ⁵³	2813	N/D	N/D
	$\nu(\text{CO})$ of terminal (t-OCH ₃)	1047 (Cu/ZrO ₂) ⁵⁴ , 1060-1070 (MgO(111)) ⁵²	1073	1062	1062
Monodentate carbonate (m-carbonate)	ν_3^b	1378 (MgO(111)) ⁵⁵ 1390 (MgO) ⁵⁶	1389	1387	1387
Bidentate carbonate	ν_3^b	1650-1730 (MgO) ^{55,57}	1700	1683	N/D
(b-carbonate)	ν_3^c	1280 (MgO) ⁵⁷ , 1270 (MgO) ⁵⁶	1266	1268	N/D

Bicarbonate	ν_4^d	1220-1250 (MgO) ³⁷	1226	1238	1230
Formic acid	$\nu(\text{C=O})$	1743 (MgO(111)) ⁵² 1729-1742 (K ₂ CO ₃ -promoted Pd/SiO ₂) ⁵⁸	1748	1748	1747
Methane	$\nu(\text{CH})$	3015 (NiFe) ⁵⁹ 2735 (NiFe) ⁵⁹ 2708 (Cu/CeO ₂) ⁶⁰ 2711 (Cu/CeO ₂) ⁶¹	3017	N/D	N/D
Formyl	$\nu(\text{CH})$	2706, 2796 (CeO ₂) ⁶² 2770, 1520 (ZnO) ⁶³ 2720, 2760, 2733 ¹⁵ 2765 ⁶⁴	N/D	2739	2734
Formaldehyde	$\nu_{as}(\text{CH}_2)$	2843 (Cu/ZnO) ⁶⁵ 2820 (SiO ₂) ⁶⁶ 2830 (SiO ₂) ⁶⁷	N/D	2843	2839
	$\nu(\text{C=O})$	1770 (Gaseous) ⁶⁶ 1725 (SiO ₂) ⁶⁷ 1761	N/D	1770	1780
Dioxymethylene on ZrO ₂	$\nu_{as}(\text{CH}_2)$	2970	2970		
	$\nu_s(\text{CH}_2)$	2870	2866		
	$2w(\text{CH}_2)$	2765	N/D	-	-
	$\delta(\text{CH}_2)$	1490	N/D		
	$w(\text{CH}_2)$	1410	1410		

^a $\nu_{as}(\text{OCO})$ increases as the Mg-O (Oxygen in formate) bond strength increases.⁴⁹

^bsymmetric stretching

^casymmetric stretching

^dCOH bending

^eNon-detectable

Supplementary note: The formation of dioxymethylene (H₂COO*) from Cu/MgOZrO₂ under H₂ flow is an important reaction intermediate and could not be excluded because the intense peak at 2866 and 1410 cm⁻¹ and its decrease was observed with time on stream. However, due to the non-detected peaks at 2870 and 2765 cm⁻¹, the formation of dioxymethylene was not mentioned in the main text.

Supplementary Table 7. Estimation of actives site quantities and TOF for Cu/MgOZrO₂ and several commercial catalysts

	Total Cu amount ($\mu\text{mol/g}_{\text{Cat}}$)	H ₂ adsorption amount ($\mu\text{mol/g}_{\text{Cat}}$) ^a	Active site (%) ^b	Cu surface area ($\text{m}^2/\text{g}_{\text{Cat}}$) ^c	Cu dispersion (%) ^d	TOF (h^{-1}) ^e
Cu/MgOZrO ₂	86.2	11.0	12.9	-	-	250 (± 12.6)
Spent Cu/MgOZrO ₂	86.2	9.8	11.5	-	-	228.4
Cu/ZrO ₂	29.1	7.1	-	-	-	-
CuO	125,700	9.8	-	-	-	-
MgOZrO ₂	0	0	-	-	-	-
HiFUEL Cu/ZnO/Al ₂ O ₃	6,688	-	-	19.7	7.3	116 (± 1.0)
Commercial Cu/ZnO/Al ₂ O ₃	7,883	-	-	33.1	10.1	101 (± 0.8)

^aObtained from consumed H₂ during H₂-TPA of the reduced catalysts.

^bQuantified by H₂ adsorption and dividing it by the total number of moles of Cu.

^cEstimated by N₂O pulse titration at 50 °C after reduction of the catalysts.

^dCalculated from Cu surface area⁶¹.

^eThe TOF of Cu/MgOZrO₂ catalysts were calculated by normalizing the activity by the quantified number active sites and the TOF of commercial CZA catalysts was estimated by normalizing the activity by the number of moles of measured Cu surface area and Cu dispersion assuming the layer of ZnO over the total Cu surface represented the actives sites^{68,69}.

Supplementary Table 8. Mean and standard deviation of the number of CO₂ molecules (μmol) during the blank test and quantity determined by three different GC measurements during CO₂ hydrogenation of Cu/MgOZrO₂.

Blank test		Measurement		
Mean	Standard deviation	1	2	3
7.912	0.02	7.801	7.813	7.814

Supplementary Table 9. Variation of products selectivity in in three measurements for Cu/MgOZrO₂ considering the unlikely case where the unclosed carbon balance is entirely due to an unknown product.

Measurement	CO ₂ conversion (%)	Carbon balance (%)	Calculated selectivity (%)			Deviation (%)
			Missing products	Methanol	CO	
1	1.393	99.70	21.0	60.1	18.9	21.0
2	1.245	99.82	13.9	65.8	20.3	13.9
3	1.240	99.82	14.0	65.7	20.3	14.0

Supplementary Table 10. Variation of products selectivity in three measurements for Cu₂L/MgOZrO₂ considering the unlikely case where the unclosed carbon balance is entirely due to an unknown product.

Measurement	CO ₂ conversion (%)	Carbon balance (%)	Calculated selectivity (%)			Deviation (%)
			Missing products	Methanol	CO	
1	1.446	100.27	-	-	-	-
2	1.948	99.76	12.2	64.6	20.2	12.1
3	1.426	100.25	-	-	-	-

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