

Selective conversion of CO₂ and H₂ into aromatics

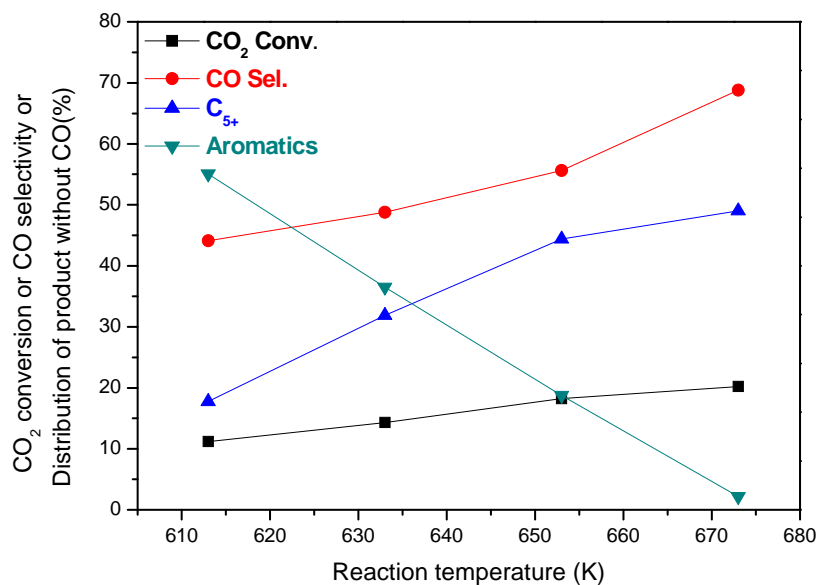
Ni et al.

Supporting information

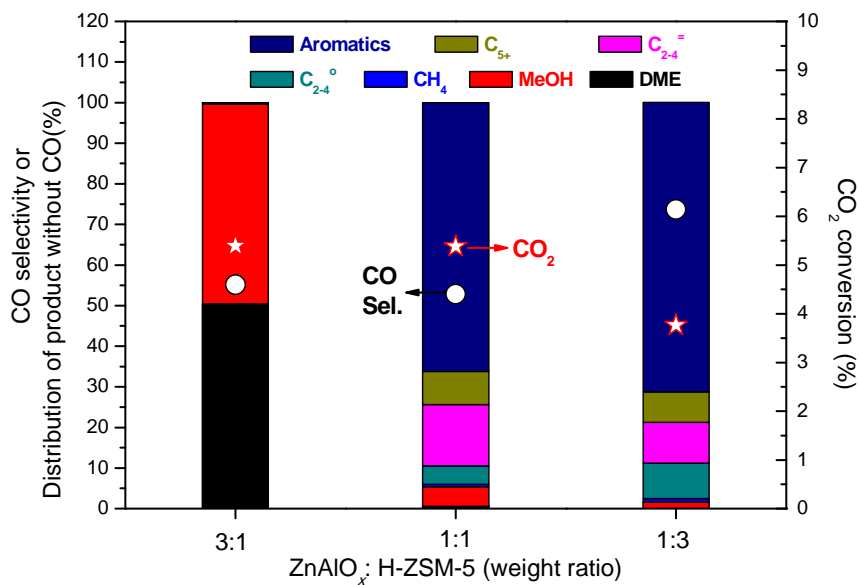
Supplementary Methods

Catalysts characterization.

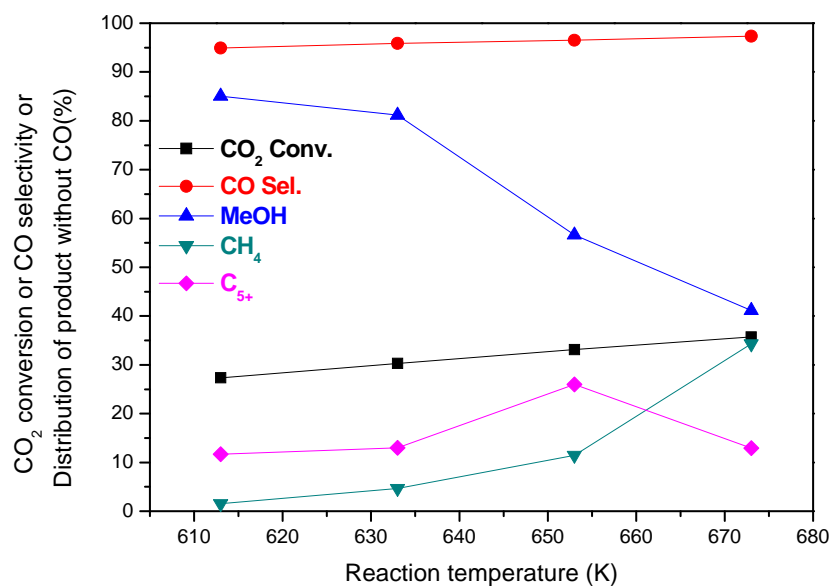
The XRD results were recorded on a PANalytical X'Pert PRO X-ray diffractometer with Cu K α radiation. The chemical composition was determined on a Philips Magix-601 X-ray fluorescence (XRF) spectrometer. SEM measurements were carried out on an SU8020 scanning electron microscopy. TEM images and element mappings were obtained on a JEM-2100 microscope at 200 kV. The BET surface areas were detected by N₂ adsorption at 77 K on a Micromeritics ASAP 2020 system and calculated by the standard multi-point method. H₂-TPR profiles were tested by a Micromeritics AutoChem II 2920 equipped with a TCD detector in a 30 ml min⁻¹ H₂/Ar (H₂/Ar=10/90) mixture with a ramping rate of 10 K min⁻¹. NH₃-TPD results were also tested by a Micromeritics AutoChem II 2920 equipped with a TCD detector. The adsorption of NH₃ was performed at 373 K in a 30 ml min⁻¹ NH₃/He (NH₃/He=5/95) mixture for 1 h, and desorption was performed in He flow by raising the temperature to 873 K at a rate of 10 K min⁻¹. *Operando* DRIFTS were detected on a Bruker Tensor 27 instrument with a MCT detector. The catalyst powder was pressed into a diffuse reflectance infrared cell with ZnSe window. First, the catalyst was treated by 30 ml min⁻¹ H₂/Ar (H₂/Ar=3/7) mixture at 593 K and 0.1 MPa for 30 min and the background spectrum was collected under the same conditions. Subsequently, 30 ml min⁻¹ mixed gas (H₂/CO₂/Ar= 3/1/0.2 or H₂/ CO/ Ar = 3/1/0.2) was introduced at 593 K and 0.1 MPa and the *operando* DRIFT spectra obtained by collecting 32 scans at 4 cm⁻¹ resolution were recorded. FTIR spectra after 2, 6-di-tert-butyl-pyridine (DTBPy) adsorption were obtained on a Bruker Tensor 27 instrument with a resolution of 4 cm⁻¹. Before each measurement, samples were pressed into a self-supporting wafer and evacuated in an IR cell at 673 K for 1 h, then cooled to 423 K and the background spectra were collected. Adsorption of DTBPy was conducted at 423 K for 15 min to ensure saturated loading and then evacuation was sufficiently carried out before each measurement.



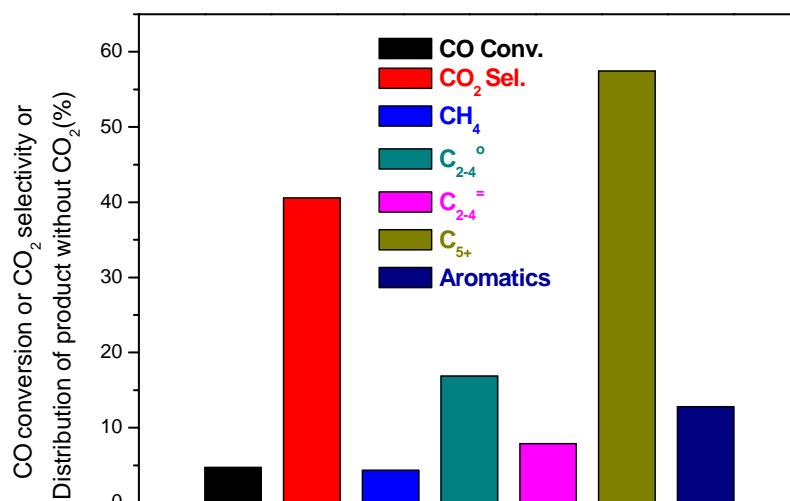
Supplementary Figure 1 | Influence of reaction temperature on the CO₂ hydrogenation over ZnAlO_x&H-ZSM-5. Reaction conditions: Space velocity = 6000 ml g⁻¹ h⁻¹, 3.0 MPa, H₂/CO₂/Ar= 3/1/0.2. Note that the C₅₊ excludes aromatics.



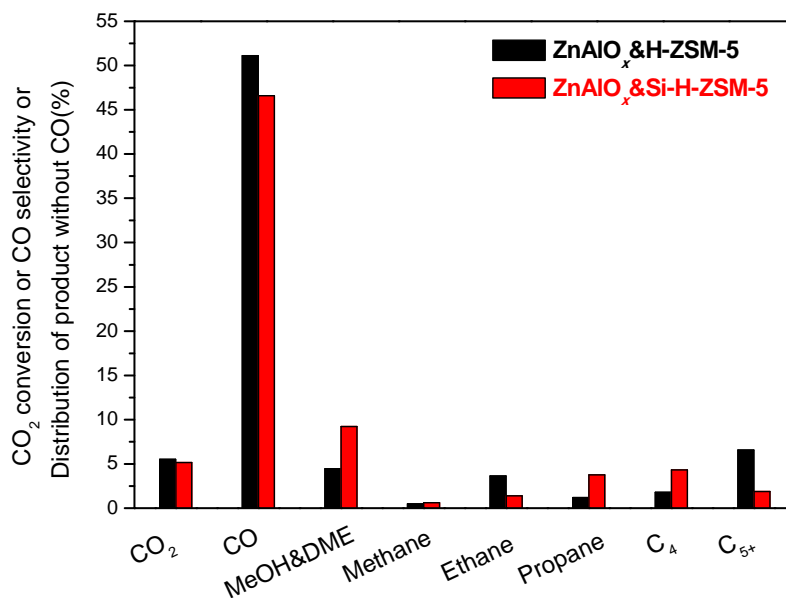
Supplementary Figure 2 | The effect of the weight ratio of Oxides/Zeolites on the CO₂ hydrogenation over ZnAlO_x&H-ZSM-5. Reaction conditions: Space velocity = 6000 ml g⁻¹ h⁻¹, 3.0 MPa, 593 K, H₂/CO₂/Ar= 3/1/0.2. Note that the C₅₊ excludes aromatics. C₂₋₄⁼ and C₂₋₄[°] refer to C₂-C₄ olefins and paraffins, respectively.



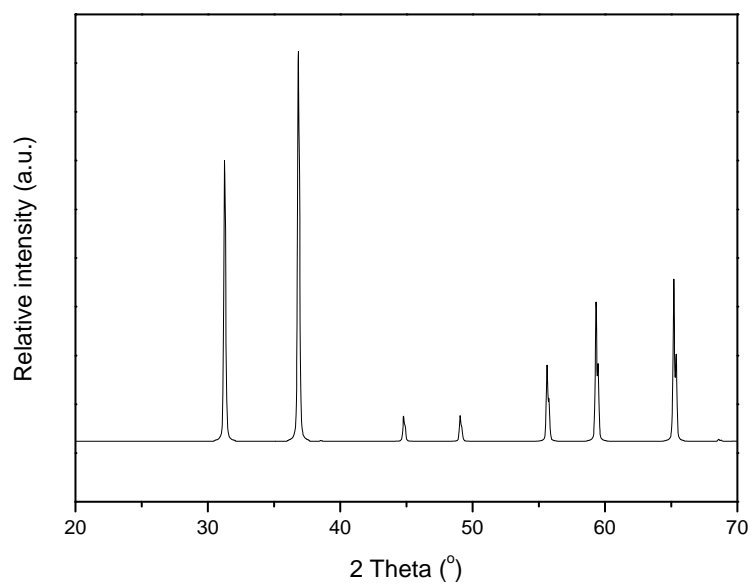
Supplementary Figure 3 | Influence of reaction temperature on the CO₂ conversion over CuZnAlO_x&H-ZSM-5. Reaction conditions: Space velocity = 5000 ml g⁻¹ h⁻¹, 3.0 MPa, H₂/CO₂/Ar= 3/1/0.2, CuZnAlO_x:H-ZSM-5 (weight ratio) = 1:1. Note that the C₅₊ excludes aromatics.



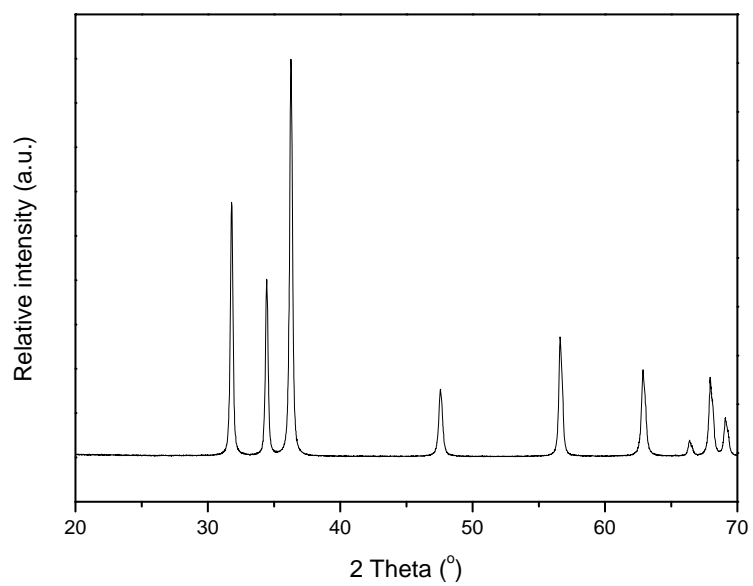
Supplementary Figure 4 | Results of the CO hydrogenation over ZnAlO_x&H-ZSM-5. Reaction conditions: Space velocity = 6000 ml g⁻¹ h⁻¹, 3.0 MPa, 593 K, H₂/CO/Ar= 3/1/0.2. Note that the C₅₊ excludes aromatics. C₂₋₄⁼ and C₂₋₄^o refer to C₂-C₄ olefins and paraffins, respectively.



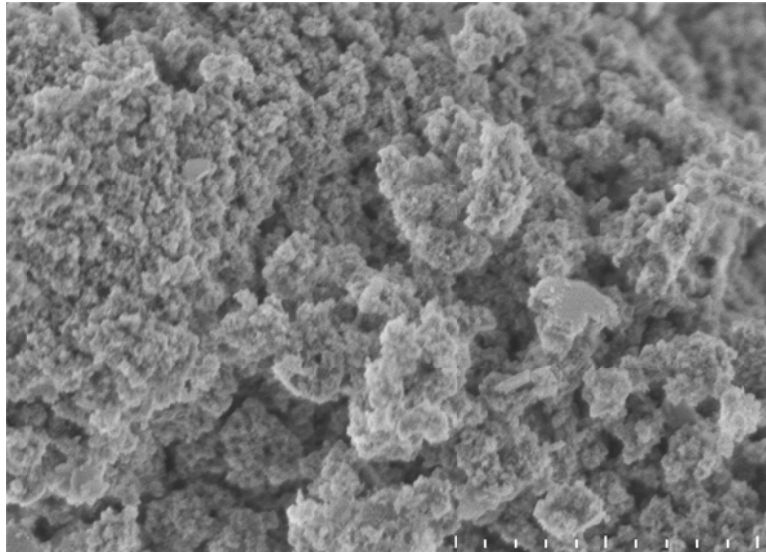
Supplementary Figure 5 | Comparisons of catalytic behaviors over ZnAlO_x&H-ZSM-5 and ZnAlO_x&Si-H-ZSM-5. Reaction conditions: Space velocity = 6000 ml g⁻¹ h⁻¹, 3.0 MPa, 593 K, H₂/CO₂/Ar= 3/1/0.2. Note that the C₅₊ excludes aromatics.¹



Supplementary Figure 6 | XRD patterns of cubic ZnAl_2O_4 gahnite.
(JCPDS 05-0669).



Supplementary Figure 7 | XRD patterns of ZnO.



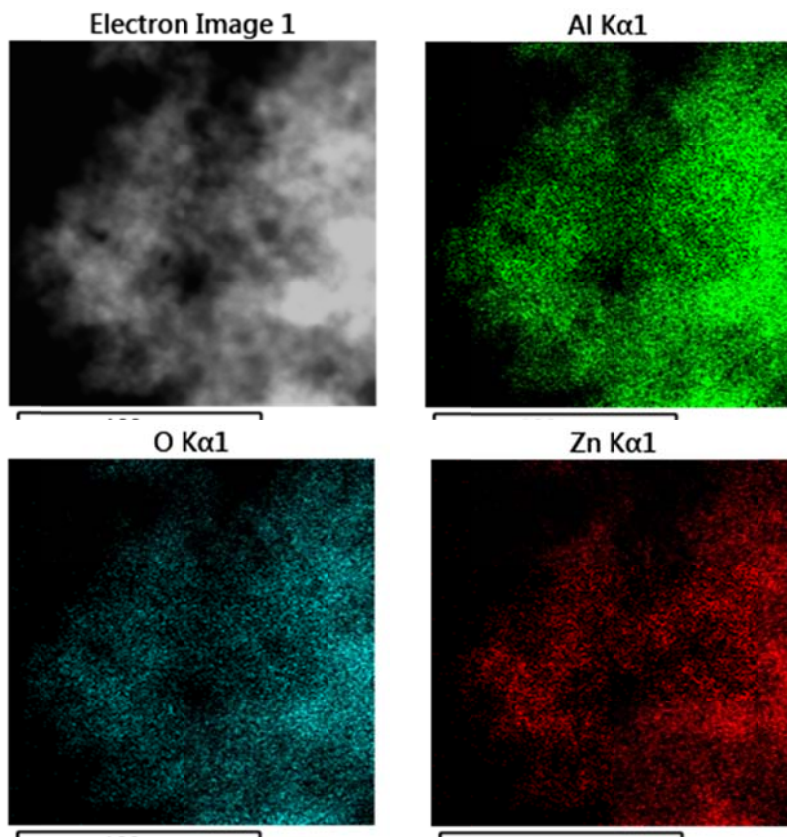
Supplementary Figure 8 | SEM image of ZnAlO_x. Scale bar: 1.0 μm.

Supplementary Table 1 | The elemental content and BET surface area for oxides

Oxides name	Zn content ^a (%)	Al content ^a (%)	BET surface area ^b (m ² g ⁻¹)
ZnAlO _x	41.5	24.5	151.0
ZnO	80.3	0	11.9

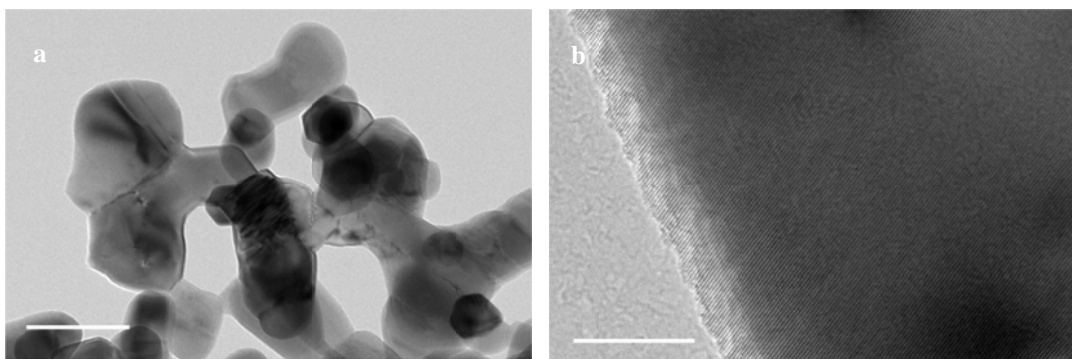
^a by XRF.

^b by N₂ physical adsorption-desorption.



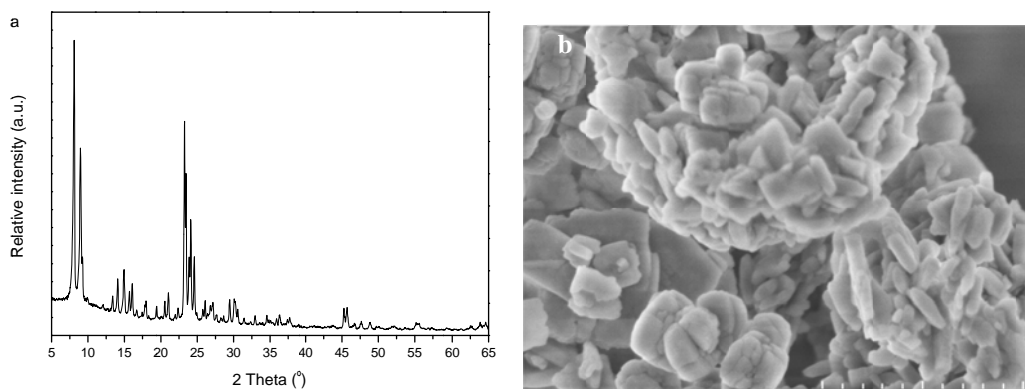
Supplementary Figure 9 | EDS mapping of Al, O, Zn for ZnAlO_x.

Scale bar: 100 nm.



Supplementary Figure 10 | TEM images of ZnO.

(a) Scale bar: 100 nm. (b) Scale bar: 10 nm.



Supplementary Figure 11 | The XRD pattern (a) and SEM image (b) of H-ZSM-5. Scale bar: 1.0 µm.

Supplementary Table 2 | The Si/Al ratio, acid content and BET surface area for zeolites

Zeolite name	Si/Al ^a (%)	Acid content ^b (mmol g ⁻¹)	BET surface area ^c (m ² g ⁻¹)
H-ZSM-5	96.6	0.109	397.0
Si-H-ZSM-5	105.8	0.085	346.8

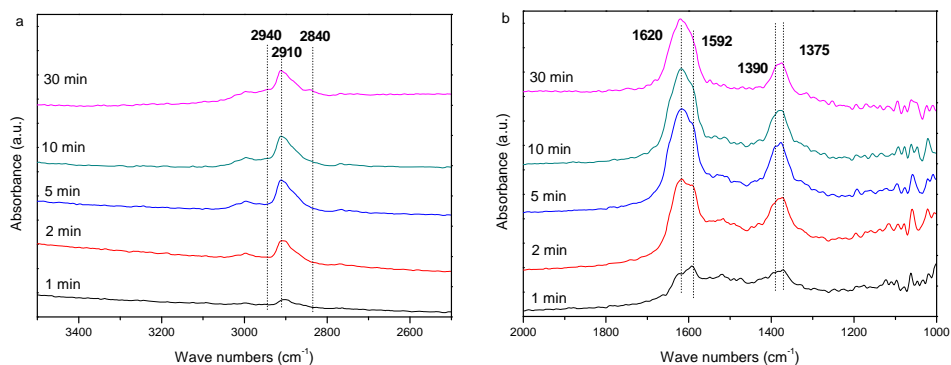
^a by XRF.

^b by NH₃-TPD.

^c by N₂ physical adsorption-desorption.

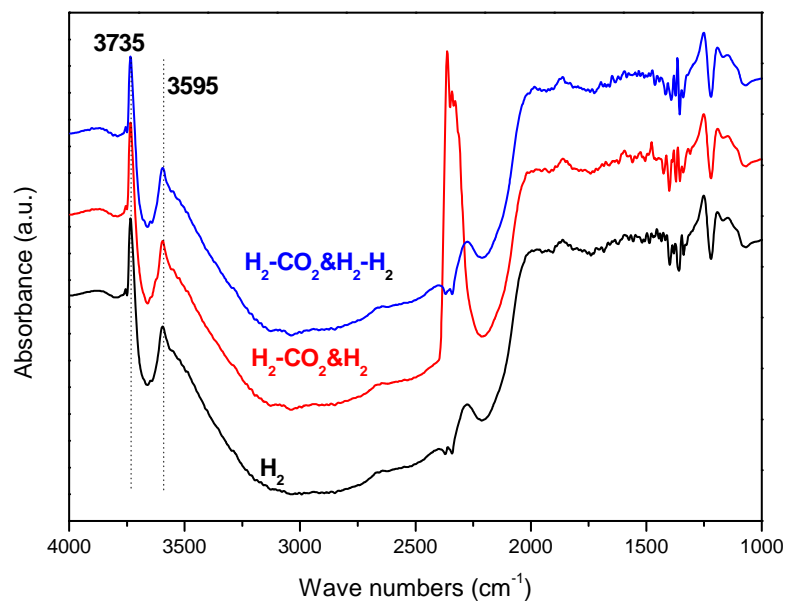
Supplementary Table 3 | The results of TPR.

Sample	Weight (mg)	Metal amount (mmol)	Peak temperature (K)	Peak area	H ₂ consumption amount (mmol)
Ag ₂ O	18.2	0.16	412.4	0.47	0.08
ZnO	201.1	2.48	852.3	0.42	0.07
ZnAlO _x	200.5	1.28	879.1	0.57	0.10



Supplementary Figure 12 | *Operando* DRIFT spectra in CO₂ hydrogenation over ZnAlO_x. Conditions: 593 K, 0.1 MPa.

The bands at 1592 and 1620 cm⁻¹ are assigned to the asymmetric stretching frequency of the O-C-O bonds of surface bidentate or monodentate formate species (HCOO), respectively. The bands at 1390 and 1375 cm⁻¹ are assigned to the symmetric stretching frequency of the O-C-O bonds of surface bidentate or monodentate formate species (HCOO), respectively. The peak at 2910 cm⁻¹ is assigned to the stretching vibration $\nu(\text{CH})$ of formate species. The bands at 2940 and 2840 cm⁻¹ are attributed to adsorbed methoxy species (CH₃O)^{1,2}.



Supplementary Figure 13 | Operando DRIFT spectra in CO₂ hydrogenation over H-ZSM-5. Conditions: 593 K, 0.1 MPa. H₂-CO₂&H₂ refers to the reaction with the mixed gas of H₂/CO/Ar= 3/1/0.2 after H₂ treatment. H₂-CO₂&H₂-H₂ refers to H₂ sweeping after H₂-CO₂&H₂ treatment.

The bands at 3735 and 3595 cm⁻¹ are assigned to silanol and bridging hydroxyls, respectively.

Supplementary References

1. Le Peltier, F., Chaumette, P., Saussey, J., Bettahar, M. M. & Lavalley, J. C. In situ FT-IR and kinetic study of methanol synthesis from CO₂/H₂ over ZnAl₂O₄ and Cu–ZnAl₂O₄ catalysts. *J. Mol. Catal. A* **132**, 91-100 (1998).
2. Mierczynski, P. *et al.* Cu/Zn_xAl_yO_z supported catalysts (ZnO: Al₂O₃=1, 2, 4) for methanol synthesis. *Catal. Today* **176**, 21-27 (2011).