

Modified Cu-Zn-Al mixed oxide dual function materials enable reactive carbon capture to methanol

Chae Jeong-Potter¹, Martha Arellano-Treviño¹, W. Wilson McNeary¹, Alexander J. Hill¹, Daniel Ruddy^{1*}, Anh To^{1*}

¹National Renewable Energy Laboratory, Catalytic Carbon Transformation and Scale-Up Center, Colorado, 80401, USA

*Corresponding authors: Anh To, anh.to@nrel.gov, Daniel Ruddy, dan.ruddy@nrel.gov

Supplemental Information

S1 Experimental

S1.1 Materials synthesis

DFMs were prepared by modifying a commercial MeOH synthesis catalyst (mixed oxide of Cu-Zn-Al, CZA, Clariant Megamax 800) with alkali and alkaline metals (Alk) using incipient wetness impregnation (incipient wetness point of CZA = 0.5 ml/g). The CZA material was crushed and sieved to 200-300 μm , and aqueous solutions of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma Aldrich) and K_2CO_3 (Sigma Aldrich) salts were used for impregnation onto the resulting powder. For every 1 g of CZA, 0.078 g of K_2CO_3 (0.56 mmol) or 0.224 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.95 mmol) was dissolved in 0.5 ml of deionized water and added dropwise to the CZA. The modified CZA DFMs (Alk/CZA, where Alk = K or Ca) were dried at 120 °C overnight (>12 h) in static air. Decomposition of the carbonate or nitrate precursors and catalyst activation were performed using in situ pre-reduction at 250 °C before characterization or activity testing. The temperature for reduction of CZA and decomposition of the precursors was informed by a temperature programmed reduction (**Figure S2**).

S1.2 Characterization

The weight loadings (wt%) of the Alk metals were determined using as-synthesized samples (i.e., after drying but before reduction to avoid the need to develop passivation/oxidation of the CZA after reduction) via inductively coupled plasma atomic emission spectroscopy (ICP-AES) at Galbraith Laboratories (Knoxville, TN).

Temperature programmed reduction in H_2 (H_2 -TPR) was performed using as-synthesized DFMs and unmodified CZA with an Altamira AMI-300Lite catalyst characterization instrument. Catalyst samples (30-50 mg) were loaded into a quartz u-tube sample cell and dried for 2 h at 100 °C in flowing Ar (25 sccm). The cell was then cooled to 30 °C in flowing Ar and 4% H_2/He was introduced at 25 sccm. The temperature was ramped from 30 °C to 250 °C at a rate of 5 °C/min and held at 250 °C for 1 h. Change in H_2 concentration was measured by an online thermal conductivity detector (TCD) and TCD intensity was normalized to actual catalyst mass.

X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV diffractometer with a Cu $\text{K}\alpha$ source. Diffractograms were collected in the 2θ range of 20–70° at a scan rate of 2°/min. XRD patterns were collected after DFM synthesis and drying.

CO₂ chemisorption was measured using an Autosorb-1-C gas sorption analyzer (Quantachrome Instruments). Approximately 200 mg of sample was diluted with 1 g of quartz chips and reduced in H₂ at 250 °C for 8 h, followed by evacuation for 8 h. CO₂ chemisorption isotherms were measured between 50 °C and 250 °C at pressures between 80 and 760 Torr in 50 Torr increments. The site density of strong CO₂ chemisorption was determined by the difference of the total and weak isotherms, extrapolated to zero pressure.

In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed using a Thermo Scientific Nicolet iS50R FT-IR spectrometer equipped with a Harrick Praying Mantis high temperature reaction chamber attachment with CaF₂ windows. The DRIFTS spectra and backgrounds were collected at a resolution of 4 cm⁻¹ with 128 scans. The samples were diluted with CaF₂ at 1:1 weight ratio and about 40-50 mg of the mixture was loaded into the sample holder on top of a small bed of silica (~50 mg). The samples were pre-reduced with 50% H₂/He at 40 sccm for 8 h at 250 °C (ramp rate: 5°C/min) before cooling to 100 °C. A background was taken for each sample after cooling to 100 °C in 40 sccm of He. The samples were exposed to 40 sccm of 5% CO₂/He for 30 min, and then purged for 1 h with 40 sccm He to remove physisorbed CO₂. Spectra were collected before and after the purge step.

SI.3 Catalytic reaction studies

SI.3.1 Fixed-bed co-fed CO₂ hydrogenation to methanol

The co-fed CO₂ hydrogenation reaction was performed in a 7.9 mm I.D. fixed-bed stainless steel reactor. Typically, 1 g of catalyst was loaded and reduced at 250 °C (ramp rate of 2 °C/min) and atm pressure for at least 16 h under 95% H₂/ 5% Ar flow (110 sccm) to decompose the carbonate or nitrate precursors and activate the catalyst. The reactor was then set to the desired reaction temperature and allowed to stabilize. Reactant flowrates for CO₂ and 95% H₂ / 5% Ar were set to achieve a total flowrate of 17 sccm and molar ratio of H₂:CO₂ = 3:1 (corresponding to WHSV of 0.5 g_{CO2} g_{cat}⁻¹ h⁻¹). Catalytic activity was monitored at 25 °C intervals from 150-250 °C and 10 bar intervals from 10-30 bar for at least 6 h at each condition.

Product analysis was performed online using an Agilent Technologies 7890B gas chromatograph equipped with flame ionization detectors (FIDs) to analyze oxygenates and HCs and TCDs to analyze permanent gases. Reactor inlet and outlet gases were sampled through heated (200 °C) lines to prevent condensation prior to analysis. The concentration of each compound was quantified by correlating its peak area with the response factor obtained from traceable gravimetric calibration standards. Ar in the inlet stream was used as an internal standard to quantify molar flowrate of all other components in the gas stream.

Conversion was calculated as:

$$\text{Conversion (\%)} = \frac{\sum \text{molar flowrate of } C \text{ in all products}}{\text{molar flowrate of inlet } CO_2} \times 100$$

C-selectivity of product *i* was calculated as:

$$C - \text{selectivity of product } i \text{ (\%)} = \frac{\text{molar flowrate of } C \text{ in product } i}{\sum \text{molar flowrate of } C \text{ in all products}} \times 100$$

SI.3.2 CO₂ adsorption – reactive desorption cycles under temperature-and-pressure-swing conditions

Performance of DFMs in the CO₂ RCC process was evaluated by conducting CO₂ adsorption – reactive desorption cycles in a Microactivity Effi unit (Micromeritics, Inc., model MME18008) under temperature-and-pressure-swing conditions. Typically, 1 g of catalyst was loaded in a 9.1 mm I.D. fixed-bed stainless steel reactor and reduced under 100 sccm of UHP H₂ at 250 °C (ramp rate of 2 °C/min) for 8 h before cooling down in 100 sccm of UHP He to 100 °C for the RCC cycle. The overall cycle conditions consisted of 4 steps (as illustrated in **Figure S4**), as following:

1. CO₂ capture: at 100 °C and 0.8 bar (atmospheric pressure in Golden, CO) for 1 h under 100 sccm of 1% CO₂/He.
2. Inert purge: at 100 °C and 0.8 bar for 1 h under 100 sccm of He. This step ensured that all weakly bound CO₂ were removed and would not contribute to the product formation during reactive desorption step.
3. Reactive desorption: flow was switched to 100 sccm of UHP H₂ and reactor was pressurized to 30 bar. After the pressure was stabilized, reactor temperature was ramped from 100-250 °C at a 5 °C/min ramp rate and hold for 2 h at high pressure (30 bar) before reducing to atmospheric pressure (0.8 bar) and hold for 1 h to clean the catalyst surface for another cycle.
4. Cool down and inert purge: at 0.8 bar under 100 sccm of He for 1 h. During this step, the reactor was cooled from 250 °C to 100 °C for the next CO₂ capture step.

The concentration of CO₂ and products were quantified on-line with a FTIR analyzer (600-HSC from California Analytical Instruments). A typical experimental procedure and associated product evolution trace is shown in **Figure S5**. A triplicate blank run was performed in identical cycle conditions as previously explained with an empty reactor tube to use as baselines. The concentration profile of each compound was integrated to quantify the total amount in μmol.

The “strong CO₂ adsorption” was quantified by CO₂ amounts in the adsorption and purge step as below. It is important to note that this “strong CO₂ adsorption” quantity excludes CO₂ consumed to produce CO during the adsorption step (step 1) and CO₂ removed during the inert purge step and (step 2) and represent quantity of CO₂ reactant for subsequent reactive desorption step (step 3).

$$\text{Strong CO}_2 \text{ adsorption} \left(\frac{\mu\text{mol}}{\text{g}} \right) = \frac{\text{Amount of CO}_{2\text{baseline}} - \text{Amount of CO}_{2\text{RCC run}} - \text{Amount of CO produced}_{\text{adsorption}}}{m_{\text{DFM}}}$$

Productivity of product *i* (including desorbed CO₂ during reactive desorption stage) was quantified as follows:

$$\text{Productivity}_i \left(\frac{\mu\text{mol}}{\text{g}} \right) = \frac{\text{Amount of } i_{\text{RCC run}} - \text{Amount of } i_{\text{baseline}}}{m_{\text{DFM}}}$$

C-selectivity of product i was quantified as follows, where j is all products from reactive desorption step, not including desorbed CO_2 and $\#C_i$ indicates the number of C in the product i molecule:

$$C\text{-Selectivity of product } i (\%) = \frac{\text{Productivity}_i \times \#C_i}{\sum (\text{Productivity}_j \times \#C_j)} \times 100$$

Conversion of adsorbed CO_2 was quantified as follows:

$$\text{CO}_2 \text{ Conversion } (\%) = \frac{\sum (\text{Productivity}_j \times \#C_j)}{\text{Strong CO}_2 \text{ adsorption}} \times 100$$

S2 Supplementary Figures

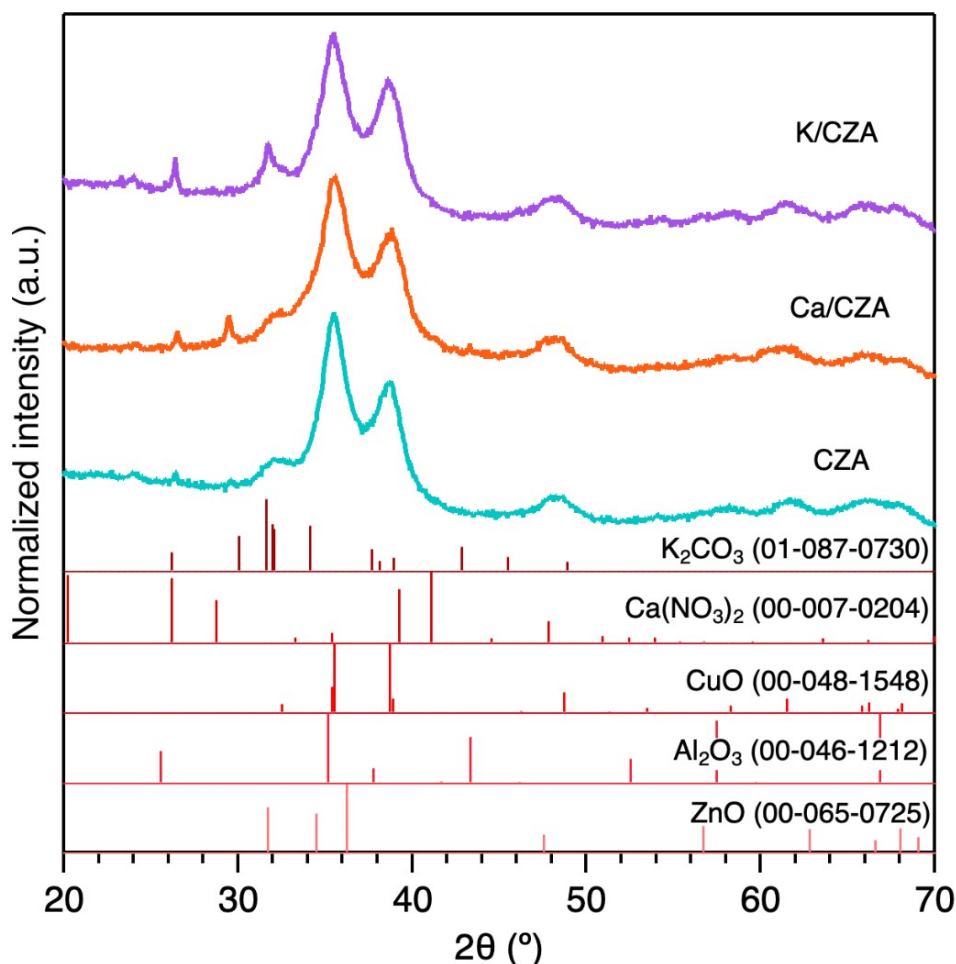


Figure S1: Powder X-ray diffraction patterns for parent CZA (teal), Ca/CZA (orange), and K/CZA (purple) after synthesis and drying. ICDD PDF card, with inset numbers, are included for the constituent metal oxides of CZA (CuO , ZnO , Al_2O_3) and Alk precursors used in DFM synthesis ($\text{Ca}(\text{NO}_3)_2$ and K_2CO_3).

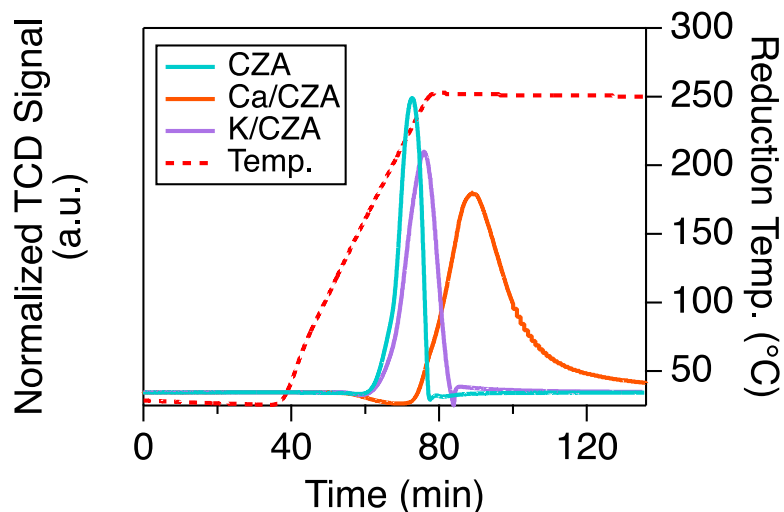


Figure S2: H₂-TPR of CZA (teal), Ca/CZA (orange), and K/CZA (purple) from 30 °C to 250 °C (red dotted line) in 4% H₂/Ar with a 1-h hold at 250 °C to show complete decomposition of alkaline precursors and reduction of CZA.

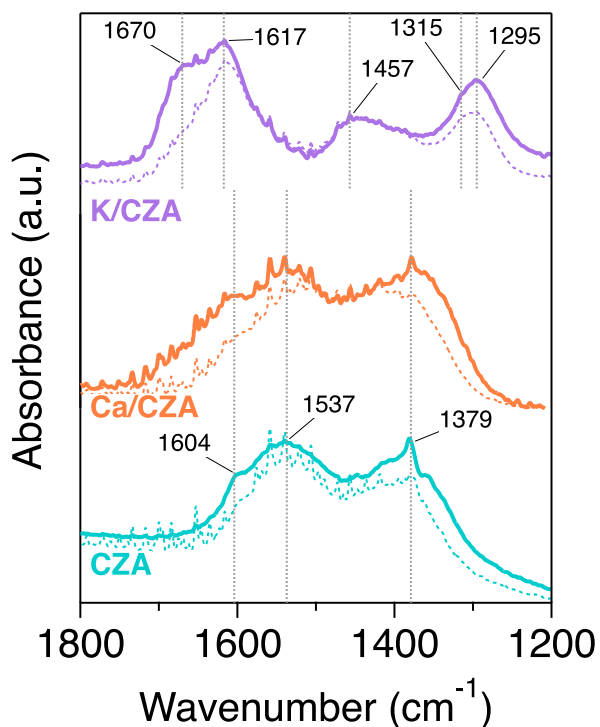


Figure S3: In-situ DRIFTS spectra of CZA (bottom, teal), Ca/CZA (middle, orange), and K/CZA (top, purple) after reduction with 50 % H₂/He at 250°C for 8 h and exposure to 5% CO₂/He at 100 °C (solid lines) prior to the inert purge. The resulting spectra following a 1-h purge with He gas is also presented for each sample (dotted lines).

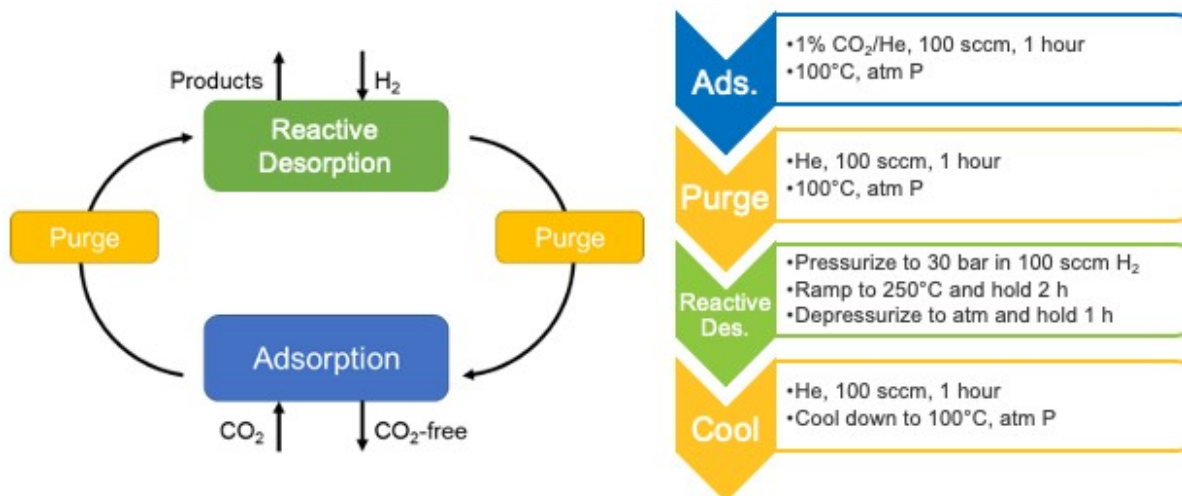


Figure S4: Graphical description of RCC cycle process steps.

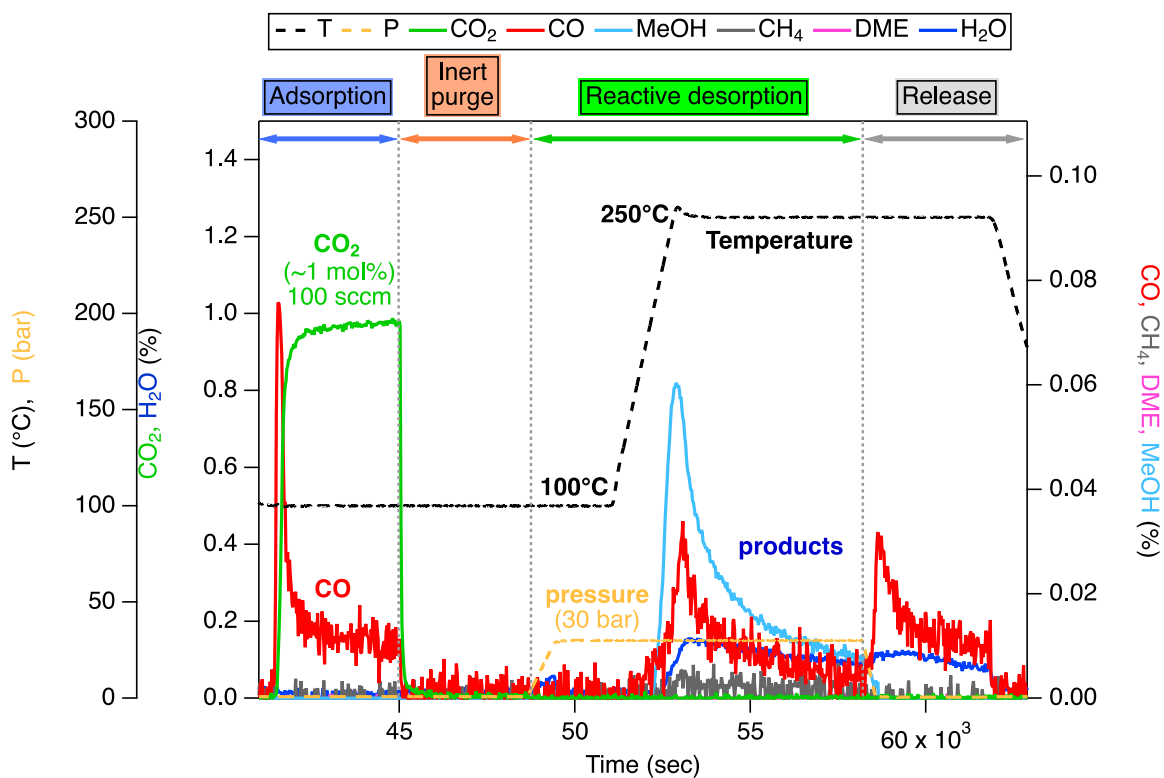


Figure S5: Typical experimental procedure and FTIR data for CO₂ capture, inert purge, and product evolution during reactive desorption (i.e., hydrogenation) in a single RCC cycle.

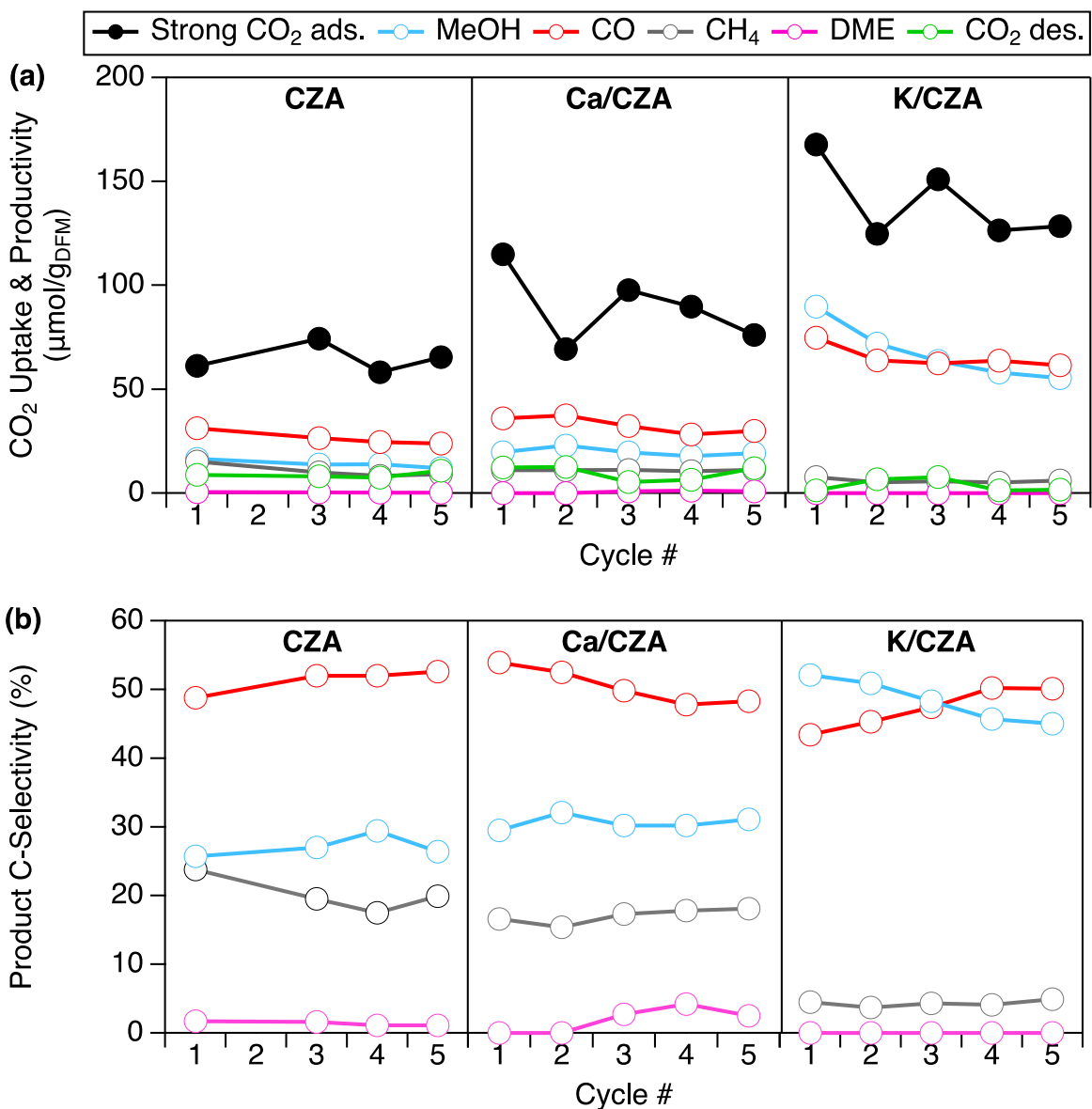


Figure S6: (a) Strong CO₂ adsorbed (black), productivity of hydrogenated products (MeOH - blue, CO - red, CH₄ - gray, DME - pink), and CO₂ desorbed (green) during 5 cycles of RCC over CZA, Ca/CZA, K/CZA. (b) Product C-selectivity over 5 cycles of RCC on each material.

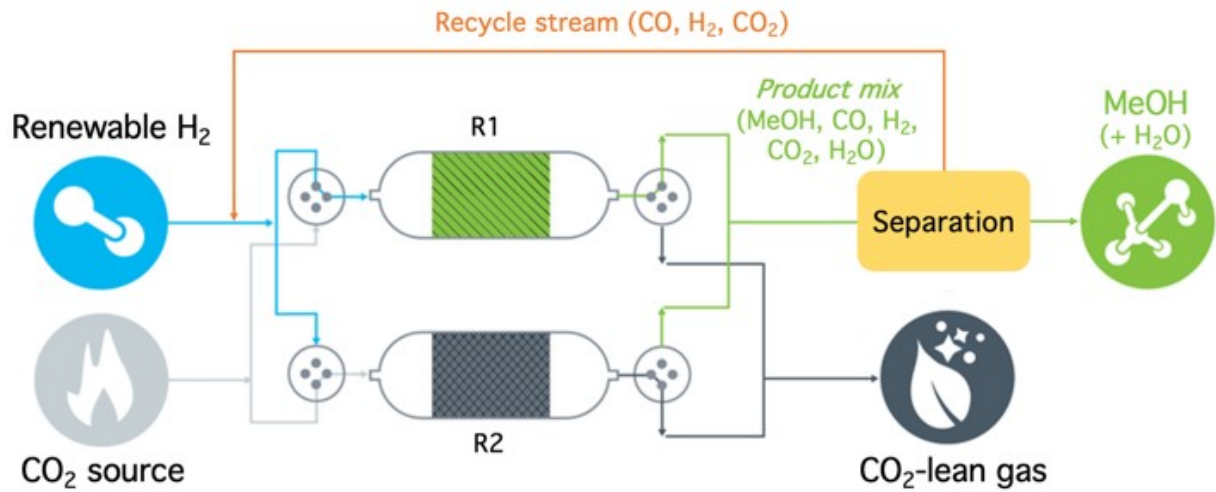


Figure S7: Conceptualized process flow diagram with product separation and recycle for RCC of CO₂ to MeOH.

S3 Supplementary Tables

Table S1: Strong chemisorbed CO₂ values for DFMs and unmodified CZA as a function of adsorption temperature from CO₂ chemisorption experiments. Percent increase in strong adsorption capacity with Alk-modification compared to the parent CZA is also included.

Adsorption Temperature (°C)	Sample	Strong CO ₂ uptake (μmol/g)	Increase in strong adsorption capacity (%)
50	CZA	132	--
	Ca/CZA	197	50
	K/CZA	265	102
100	CZA	126	--
	Ca/CZA	171	35
	K/CZA	278	120
150	CZA	124	--
	Ca/CZA	157	26
	K/CZA	282	128
200	CZA	74	--
	Ca/CZA	144	95
	K/CZA	260	253
250	CZA	42	--
	Ca/CZA	105	148
	K/CZA	206	389

Table S2: Peak positions of observed surface species on CZA, Ca/CZA, and K/CZA after 30 minutes of exposure to 5% CO₂/He at 100 °C followed by an inert purge. Peak positions of monodentate geometry on Ca/CZA are indicated in parenthesis "()" to indicate that this species may exist but is coincident with bridged bidentate species on unmodified CZA.

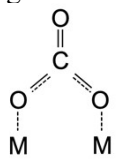
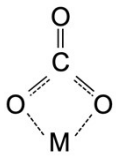
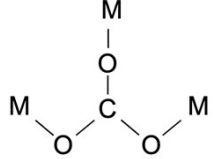
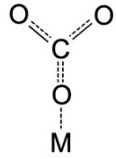
Surface Species	CZA	Ca/CZA	K/CZA
Bridged bidentate 	1604 cm ⁻¹ 1379 cm ⁻¹	--	1670 cm ⁻¹ 1295 cm ⁻¹
Chelating bidentate 	--	--	1617 cm ⁻¹ 1315 cm ⁻¹
Polydentate 	1537 cm ⁻¹	--	1457 cm ⁻¹
Monodentate 	--	(1630 cm ⁻¹) (1340 cm ⁻¹)	--

Table S3: Conversion and product C-selectivity for CZA, Ca/CZA, and K/CZA over a range of reaction temperatures and pressures (T = 150–250 °C, P = 10 - 30 bar) in the co-fed CO₂ hydrogenation reaction. Reaction conditions: WHSV = 0.5 g_{CO2} g_{cat}⁻¹ h⁻¹, CO₂:H₂ = 3:1. Standard deviations provided for CO₂ conversion values.

Reaction Condition	Sample	Conversion (%)	Product C-Selectivity (%)			
			MeOH	CO	CH ₄	C ₂₊
150 °C 30 bar	CZA	10.1 ± 0.3	94.6	5.4	0	0
	Ca/CZA	4.2 ± 0.9	99.9	0	0	0.06
	K/CZA	0	--	--	--	--
175 °C 30 bar	CZA	19.5 ± 0.5	84.6	94.6	0	0
	Ca/CZA	9.6 ± 0.5	93.9	6.1	0	0
	K/CZA	0.4 ± 0.1	24.4	74.6	0.7	0.4
200 °C 30 bar	CZA	26.6 ± 1.1	79.1	20.9	0	0
	Ca/CZA	18.7 ± 0.7	78.4	21.5	0	0.07
	K/CZA	1.3 ± 0.1	7.0	91.0	1.5	0.4
225 °C 30 bar	CZA	39.9 ± 1.1	80.8	19.1	0	0
	Ca/CZA	30.0 ± 1.2	69.3	30.6	0	0.1
	K/CZA	5.5 ± 0.1	2.8	95.3	1.4	0.5
250 °C 30 bar	CZA	34.2 ± 0.6	62.6	37.2	0.2	0.2
	Ca/CZA	33.4 ± 1.3	63.1	36.4	0	0.4
	K/CZA	16.2 ± 0.2	2.2	95.6	1.6	0.7
250 °C 20 bar	CZA	29.8 ± 1.1	48.0	51.8	0.1	0.1
	Ca/CZA	33.4 ± 1.3	63.1	36.4	0	0.4
	K/CZA	16.2 ± 0.2	2.2	95.6	1.6	0.7
250 °C 10 bar	CZA	22.4 ± 1.1	17.4	75.9	6.7	0
	Ca/CZA	21.8 ± 0.3	19.6	80.1	0	0.3
	K/CZA	16.2 ± 0.2	2.2	95.6	1.6	0.7

Table S4: Amount of strong CO₂ adsorbed, CO produced, and their ratios during CO₂ adsorption and inert purge steps of the RCC cycles (T = 100 °C, P = 0.8 bar). The data presented are averages of the last 3 cycles with standard deviations.

Sample	Strong CO ₂ adsorbed (μmol/g)	CO produced (μmol/g)	CO produced/strong CO ₂ adsorbed
CZA	66.0 ± 6.6	46.1 ± 0.6	0.70
Ca/CZA	87.8 ± 8.9	15.4 ± 0.7	0.18
K/CZA	135.3 ± 11.1	11.4 ± 1.0	0.08

Table S5: Conversion of adsorbed CO₂ to products, amount of CO₂ desorbed, and product C-selectivity during each stage of the reactive desorption step. The data presented are averages of the last 3 cycles.

Cycle step	Sample	CO ₂ conversion (%)	Desorbed CO ₂ amount (μmol/g)	Product C-selectivity (mol %)			
				MeOH	CO	CH ₄	DME
Hydrogenation at 30 bar	CZA	40.1	7.97	49.1	17.2	31.3	2.3
	Ca/CZA	38.0	7.01	55.5	11.8	28.6	4.0
	K/CZA	73.0	3.29	58.5	35.9	5.6	0.0
Pressure release and hold at 0.8 bar	CZA	33.0	0.79	1.5	94.6	3.9	0.0
	Ca/CZA	33.2	0.89	1.8	90.8	5.3	2.1
	K/CZA	21.4	0.26	5.0	94.5	0.5	0.0
Combined	CZA	73.1	8.77	27.6	52.2	19.0	1.2
	Ca/CZA	71.2	7.90	30.5	48.6	17.7	3.1
	K/CZA	94.4	3.55	46.3	49.2	4.4	0.0