# Supporting information

**Reactive Direct Air Capture of CO$_2$ to C-C Coupled Products using Multifunctional Materials**

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**S1. Experimental**

**S1.1 Chemicals**

High surface area $\gamma$-Al$_2$O$_3$ was supplied by Saint Gobin Norpro. Fe(NO$_3$)$_3$.9H$_2$O, Co(NO$_3$)$_2$.6H$_2$O K$_2$CO$_3$, and glucose were purchased from Sigma Aldrich. Activated carbon (AC), darco G-60 was received from Fisher Scientific. Fe$_2$O$_3$ was purchased from Thermo Scientific Chemicals.

**S1.2 Preparation of Sorbents and Sorbent-Catalytic Materials**

25 wt% K$_2$CO$_3$/Al$_2$O$_3$ and K$_2$CO$_3$/AC were synthesized using wet impregnation method by mixing the Al$_2$O$_3$ or AC to an aqueous solution of K$_2$CO$_3$ followed by stirring at room temperature for 10 h. The samples were dried in an oven at 105 °C followed by calcination at 300 °C for 2 h for K$_2$CO$_3$/Al$_2$O$_3$.[1]

The Fe$_2$O$_3$-K$_2$CO$_3$/Al$_2$O$_3$ (Fe-KA) was prepared by simple physical mixing in a mortar-pestle, keeping the mole ratio of Fe$_2$O$_3$: K$_2$CO$_3$ = 1:1.

The Fe/C was synthesized following the hydrothermal synthesis method[2] by mixing Fe(NO$_3$)$_3$.9H$_2$O with glucose in 1:1 mole ratio in deionized water. After stirring for 1 h, the mixture was heated at 150 °C for 24 h in a closed vessel. The resulting solid was filtered and washed with 750 mL H$_2$O and 75 mL ethanol followed by drying at 120 °C for 10 h. 25 wt% of K$_2$CO$_3$ was impregnated on Fe/C following the similar method to K$_2$CO$_3$/Al$_2$O$_3$, denoted as K$_2$CO$_3$/Fe/C. Prior to CO$_2$ capture, the K$_2$CO$_3$/Fe/C was pretreated under H$_2$ (60 mL/min) for 10 h at 400 °C to ensure carbide formation.

40 wt% of $Al_2O_3$ and 35 wt% of Fe/C was mixed with 100 mL of water followed by impregnation of 25 wt% $K_2CO_3$ and stirring for 10 h. The samples were dried in an oven at 110 °C to evaporate the water. The samples were denoted as $K_2CO_3$/Fe/C/$Al_2O_3$.

The Fe-Co/$K_2CO_3$/$Al_2O_3$ (Fe-Co/KA) and Fe/$K_2CO_3$/$Al_2O_3$ (Fe/KA) were synthesized by wet impregnation method[3]. The $Fe(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$ were dissolved in water and 25wt% of $K_2CO_3$/$Al_2O_3$ was added to the solution. The mixture was stirred at 60 °C for 4 h followed by drying at 100 °C overnight. The sample was calcined at 500 °C for 4 h. The calcined sample was placed in a Parr reactor, pressurized with 250 psi of $CO_2$ and left for 16 h at room temperature to convert any $K_2O$ formed during the reaction back to $K_2CO_3$. 12.4 wt% Fe and 2.6 wt% Co was impregnated. The resulting sample is named as Fe-Co/$K_2CO_3$/$Al_2O_3$ (Fe-Co/KA). 12.4 wt% Fe/$K_2CO_3$/$Al_2O_3$ (Fe/KA) was also synthesized is the similar way.

**S1.3 Catalyst Characterization**

Powder X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer, Rigaku Smartlab SE diffractometer CuKα radiation (40 kV, 44 mA). $N_2$ adsorption–desorption experiments were conducted at −196°C (Quadrasorb automated area and pore size analyzer). Specific surface areas and pore diameters were estimated with the Brunauer−Emmett−Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method, respectively. The samples were heated under vacuum at 120 °C for 4 h to remove any physisorbed water (Masterprep multi-zone flow/vacuum degasser). Temperature program desorption (TPD) (Micromeritics AutoChem II) was carried out under the flow of He (10 mL/min) for both fresh and spent samples from 40 to 500 °C (5 °C/min). FTIR spectra of the samples were collected using a DRIFTS cell and Nicolet is50 FTIR Spectrometer using an MCT detector.

**S1.4 $CO_2$ Capture and Catalytic Evaluation**

The investigation on integrated $CO_2$ capture and hydrogenation was performed using the experimental setup shown in Scheme S1. The setup consists of three MFCs connected to a fixed bed flow reactor and an evaporator for introducing water vapor. 2 g of sorbent or sorbent-catalyst (sorb-cat) in powder form was used for each run. The materials were either pretreated at 200 °C for 1 h under $N_2$ flow (100 mL/min.) or 400 °C under $H_2$ flow at 60 mL/min flow rate for 5 h. Integrated $CO_2$ capture and conversion involves two key steps:

1. $CO_2$ capture was performed at 25 °C in presence of 0.5 mol% $H_2O$ vapor. The carbonation reaction was carried out by co-feeding 400 ppm of $CO_2$ at 1200 mL/min along with 0.5 mol% $H_2O$ vapor at 25 °C over the sorbent or sorb-cat bed for 4 h. The $CO_2$ adsorbed was analyzed by $CO_2$ analyzer, Model 906 equipped with an NDIR sensor. In a different set of reaction, the target material was first pre-saturated with 0.5 or 1.0 mol% of $H_2O$ vapor for 2 h followed by co-feeding $CO_2$ (400 ppm, 1200 mL/min) (in $N_2$) with $H_2O$ vapor (0.5 mol%) for 4 h.

2. Reduction of the captured $CO_2$ was carried out under $H_2$ flow of 60 mL/min, 1.0 MPa and at 320 and 360 °C. The product gases were analyzed by four-channel Inficon micro-GC fusion with a TCD detector.
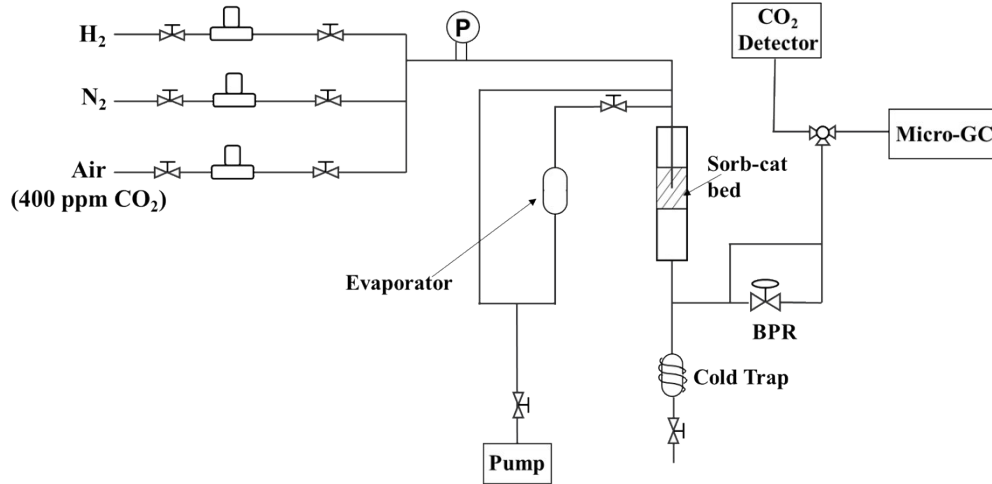
**Scheme S1:** Set-up for direct air capture (DAC)

The calculation of the molar quantity of the $CO_2$ adsorbed, *denoted as $n_{CO2}$* per gram of sorbent, was performed by integrating the molar concentration curve (derived from $CO_2$ ppm vs. time data, as shown in Figure S2) over the $CO_2$ capture time ($F_{CO2}$, 4h), and then divided by the mass of the sorbent (*W), as* shown in the equation below:

$$n_{CO2} = 1/W \int_{t_0}^{t_4} F_{CO2}(t)d \qquad (1)$$

DAC and Conversion:

The $CO_2$ conversion ($X_{CO2}$) and the selectivity (S) of each product (x) were calculated using the following equations:

$$X_{CO2} = \frac{n_{total\ products}}{n_{CO2\ adsorbed}} \times 100\% \qquad (2)$$

$$S_x = \frac{n_x}{n_{total\ products}} \times 100\% \qquad (3)$$

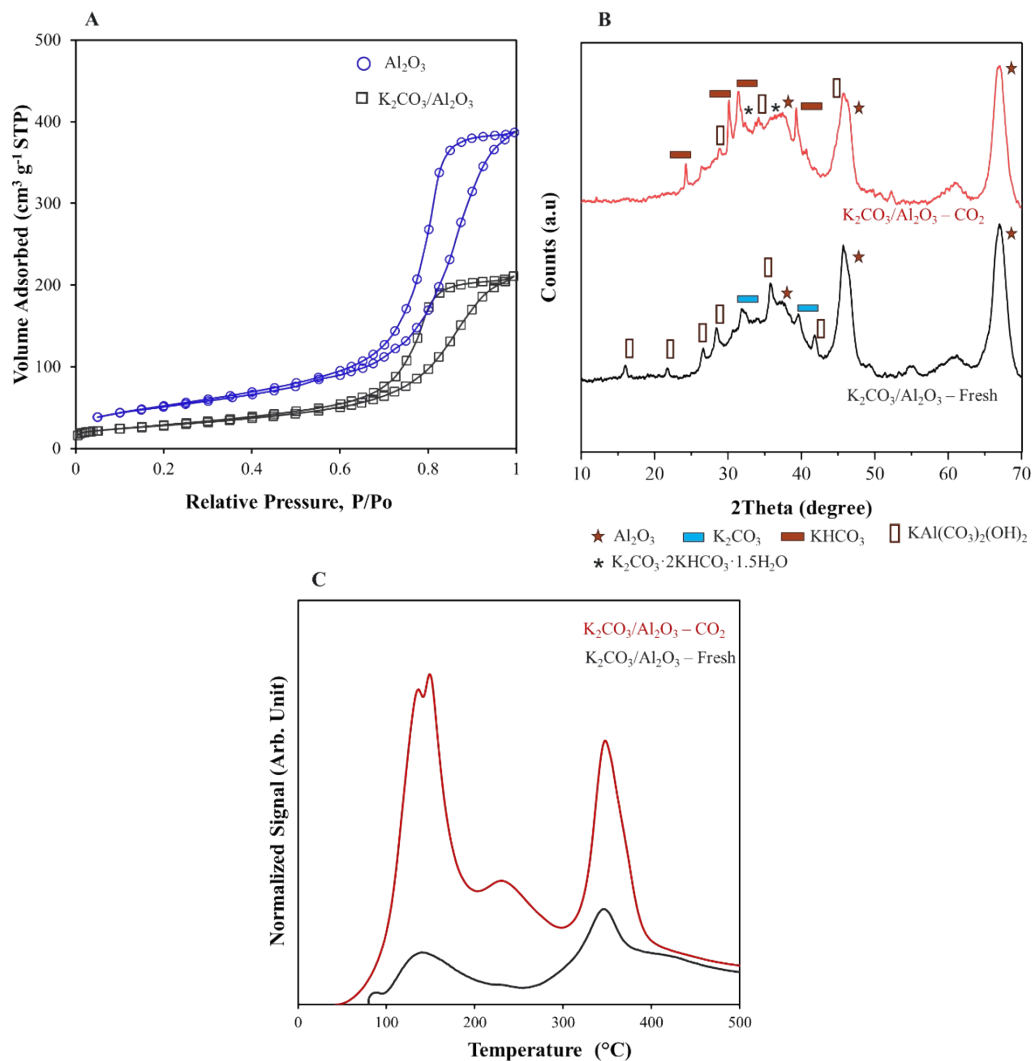where n is the number of moles of the components identified from the outlet gases.

Gas phase $CO_2$ Conversion:

The $CO_2$ conversion ($X_{CO2}$) and the selectivity (S) of each product (x) were calculated using the following equations:

$$X_{CO2} = \frac{n_{total\ products}}{n_{inlet\ CO2}} \times 100\% \qquad (4)$$

$$S_x = \frac{n_x}{n_{total\ products}} \times 100\% \qquad (5)$$

## S2. Results



**Figure S1: (A)** Nitrogen adsorption-desorption isotherm of $Al_2O_3$ and $K_2CO_3/Al_2O_3$ **(B)** Wide angle XRD of fresh and $CO_2$ captured $K_2CO_3/Al_2O_3$ **(C)** TPD of fresh and $CO_2$ captured $K_2CO_3/Al_2O_3$.

XRD of the $CO_2$ captured sample in Figure S1B shows the characteristic narrow diffraction peaks for $KHCO_3$ (ICDD PDF-2 #13-5503). The peaks for dawsonite in the $CO_2$ captured sample is broader compared to the fresh one, which indicates that the introduction of 400 ppm $CO_2$ through the sample in presence of water vapor gives rise to formation

of more dawsonite. Small, broad peaks were also visible confirming the presence of $K_2CO_3 \cdot 2KHCO_3 \cdot 1.5H_2O$ (ICDD PDF-2 #20-0886).[4, 5]

**Table S1**: Physicochemical properties of $Al_2O_3$ and $K_2CO_3/Al_2O_3$.

|  | SA ($m^2/g$) | PV ($cm^3/g$) | Average Diameter (nm) |
|---|---|---|---|
| $Al_2O_3$ | 182.4 | 0.6001 | 11.4 |
| $K_2CO_3/Al_2O_3$ | 99.19 | 0.3262 | 10.09 |
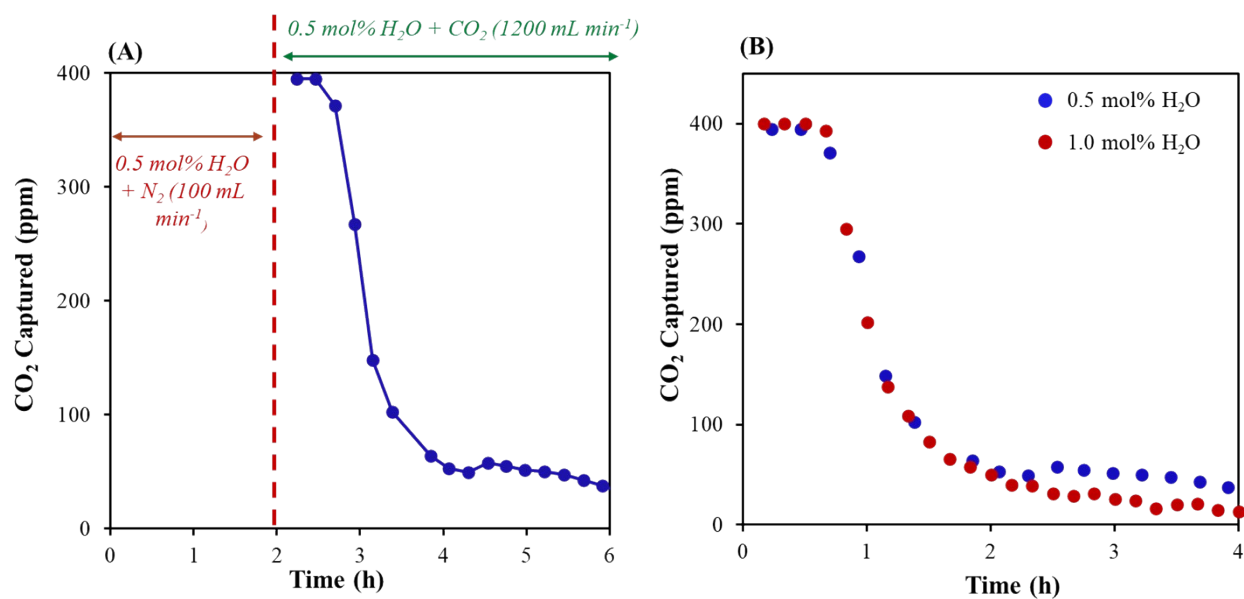


**Figure S2: (A)** $CO_2$ capture profile for $K_2CO_3/Al_2O_3$ pre-saturated with 0.5 mol% $H_2O$ followed by co-feeding $CO_2$ with $H_2O$ vapor, **(B)** Comparison of $CO_2$ capture profile for $K_2CO_3/Al_2O_3$ pre-saturated with 0.5 and 1.0 mol% of $H_2O$ vapor.

Amount of material: 2 g; Pretreatment conditions: $N_2$ = 100 mL/min, 200 °C, 1 h; $CO_2$ capture conditions: $CO_2$ = 400 ppm in $N_2$ (flow rate = 1200 mL/min), $H_2O$ vapor = 0.5 mol%, 25 °C, 4 h.
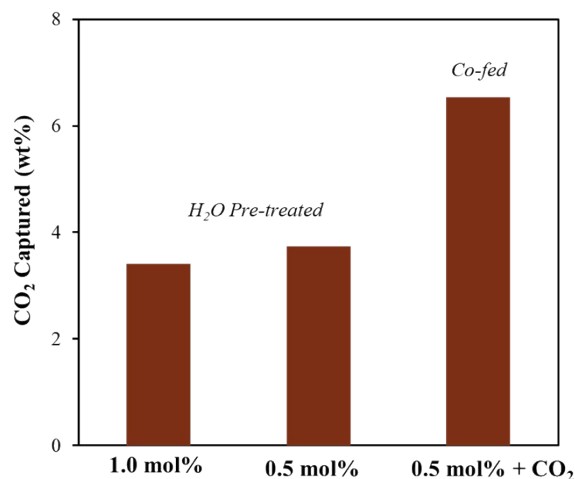
**Figure S3:** Comparison of $CO_2$ capture capacity in wt% for $K_2CO_3/Al_2O_3$ under different conditions. Amount of material: 2 g; Pretreatment conditions: $N_2$ = 100 mL/min, 200 °C, 1 h; $CO_2$ capture conditions: $CO_2$ = 400 ppm in $N_2$ (flow rate = 1200 mL/min), $H_2O$ vapor = 0.5 mol%, 25 °C, 4 h.

For the $H_2O$ vapor-pretreated samples, $K_2CO_3/Al_2O_3$ was first saturated with 0.5 and 1.0 mol% $H_2O$ vapor for 2 h followed by co-feeding $CO_2$ (400 ppm in $N_2$) with $H_2O$ vapor (0.5 and 1.0 mol%) for 4 h. For the co-fed experiment, 0.5 mol% $H_2O$ vapor was co-fed with 400 ppm of $CO_2$ over $K_2CO_3/Al_2O_3$ for 6 h.
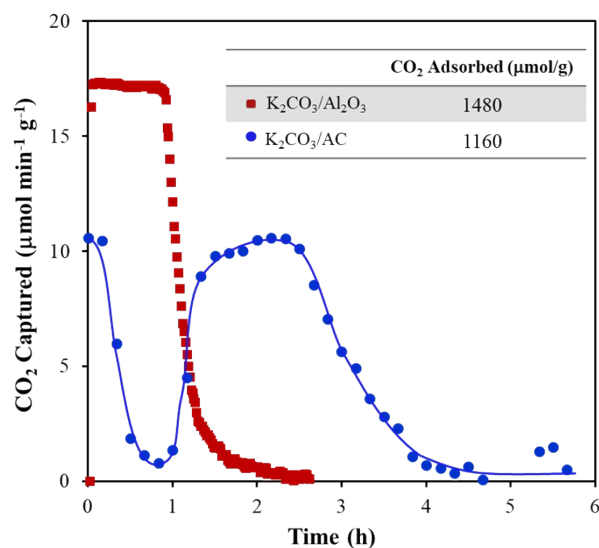


**Figure S4:** $CO_2$ capture profile in molar flow concentration versus time for $K_2CO_3/Al_2O_3$ and $K_2CO_3/AC$. Amount of material ($K_2CO_3/Al_2O_3$ or $K_2CO_3/AC$): 2 g; Pretreatment conditions: $N_2$ = 100mL/min, 200 °C, 1 h; $CO_2$ capture conditions: $CO_2$ = 400 ppm in $N_2$ (flow rate = 1200 mL/min), $H_2O$ vapor = 0.5 mol%, 25 °C, 4 h

**Table S2:** $CO_2$ Sorption Capacity of the Sorb-Cat materials.

| Materials | Pretreatment Conditions | $CO_2$ Captured (μmol/g) | $K_2CO_3$ (μmol/g) | $CO_2$ Desorbed (μmol/g) |
|---|---|---|---|---|
| $K_2CO_3/Al_2O_3$ | $N_2$, 200 °C, 1 h | 1487 | 1820 | N/A |
| $K_2CO_3/Al_2O_3$ | $H_2$, 400 °C, 5h | 1862 | 1820 | N/A |
| $Fe_2O_3$-KA (PM) | $N_2$, 200 °C, 1 h | 591 | 1750 | 1082 |
| $Fe_2O_3$-KA (PM) | $H_2$, 400 °C, 5 h | 1420 | 1750 | 1220 |

Amount of material: 2 g; $CO_2$ capture conditions: $CO_2$ = 400 ppm in $N_2$ (flow rate = 1200 mL/min), $H_2O$ vapor = 0.5 mol%, 25 °C, 4 h; Hydrogenation: $H_2$ = 60 mL/min, 1.0 MPa, 320 °C for 2.5 h (5 °C/min), followed by heating to 360 °C (5 °C/min) for 2 h.

**Table S3:** Comparison of the $CO_2$ capture capacity of $K_2CO_3/Al_2O_3$ and Fe/KA for two cycles.
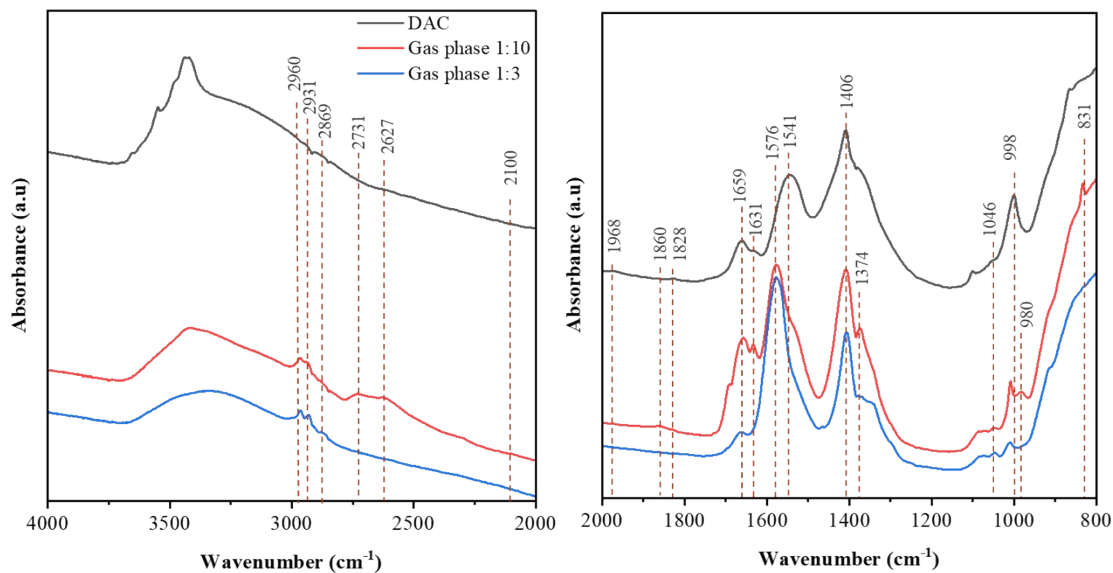
| Entry | Material | | Pretreatment Condition | $CO_2$ Capture Capacity (μmol/g) | Capture Capacity (wt%) |
|---|---|---|---|---|---|
| 1 | Fresh $K_2CO_3/Al_2O_3$[a] | Cycle 1 | $N_2$ (100 mL/min), 200 °C, 1 h | 1487 | 6.5 |
| | Spent $K_2CO_3/Al_2O_3$ [a] | Cycle 2 | $N_2$ (100 mL/min), 200 °C, 1 h | 1203 | 5.3 |
| | $K_2CO_3/Al_2O_3$ | Cycle 1 | $H_2$, 400 °C, 5h | 1862 | 8.2 |
| 2 | Fe/KA [a] | Cycle 1 | $H_2$ (60 mL/min), 400 °C, 5 h | 1645 | 7.4 |
| | Fe/KA (spent) [a] | Cycle 2 | $H_2$ (60 mL/min), 320 °C for 2.5 h and 400 °C for 2.5 h | 1276 | 5.6 |
| 3 | $K_2CO_3/Al_2O_3$ (unmodified $Al_2O_3$) | | Ar (100 mL/min), 200 °C, 1 h | ~ 826 | 3.6 |
| | $K_2CO_3/Al_2O_3$-750 (Thermally modified $Al_2O_3$) | Literature[4] | | ~ 938 | 4.1 |

Amount of material: 2 g; $CO_2$ capture conditions for entries 1 and 2: $CO_2$ = 400 ppm in $N_2$ (flow rate = 1200 mL/min), $H_2O$ vapor = 0.5 mol%, 25 °C, 4 h.
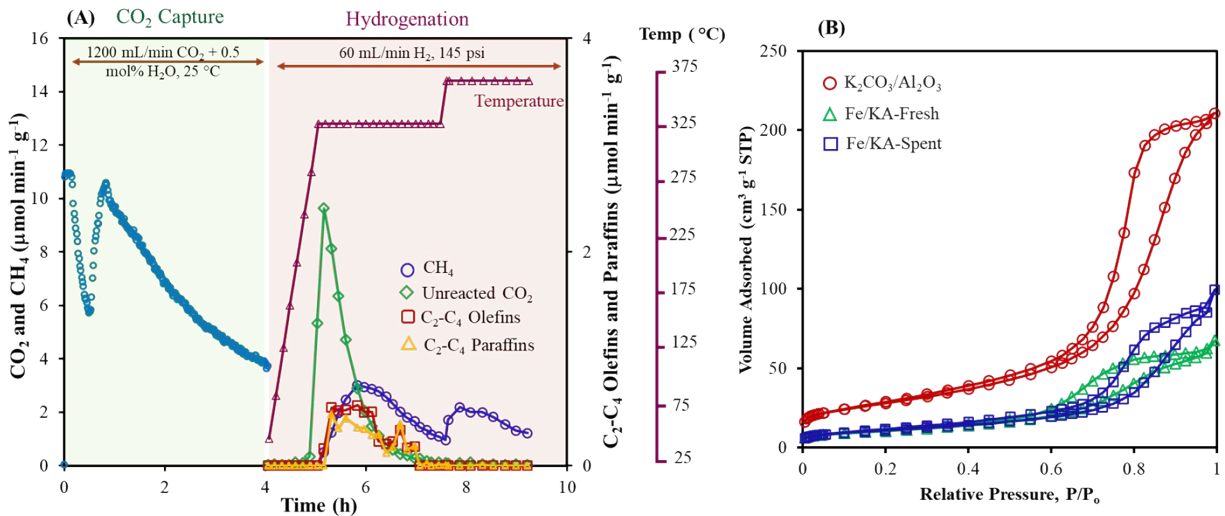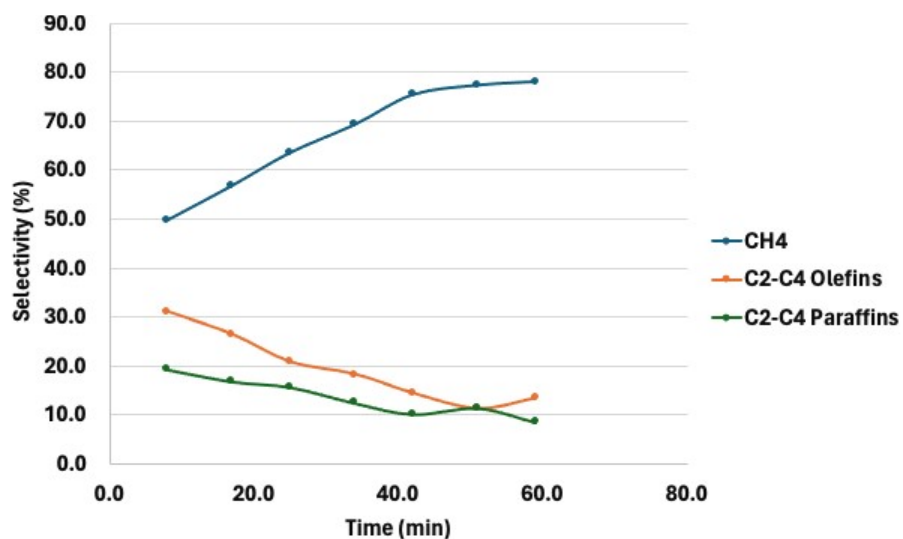
**Figure S5: (A)** $CO_2$ capture followed by hydrogenation of captured $CO_2$ over Fe/KA, **(B)** $N_2$ adsorption-desorption isotherm of $K_2CO_3/Al_2O_3$, Fe/KA-Fresh and Fe/KA-Spent samples.

Fe/KA: 2 g; Pretreatment conditions: $H_2$ = 60 mL/min, 400 °C, 5 h; $CO_2$ capture conditions: $CO_2$ = 400 ppm in $N_2$ (flow rate = 1200 mL/min), $H_2O$ vapor = 0.5 mol%, 25 °C, 4 h; Hydrogenation: $H_2$ = 60 mL/min, 1.0 MPa, 320 °C for 2.5 h (5 °C/min), followed by heating to 360 °C (5 °C/min) for 2 h.



**Figure S6:** FTIR spectrum of spent samples of Fe/KA for DAC and gas phase $CO_2$ reactions.

**Figure S7:** Hydrogenation of $CO_2$ captured in $H_2/CO$ pretreated Fe/KA (Table 2) at 320 °C. Amount of material: 2 g; Pretreatment conditions: $H_2/CO$ (2:1) = 60 mL/min, 400 °C, 3 h, followed by $H_2$ = 60 mL/min, 400 °C, 5 h; $CO_2$ capture conditions: $CO_2$ = 400 ppm in $N_2$ (flow rate = 1200 mL/min), $H_2O$ vapor = 0.5 mol%, 25 °C, 4 h; Hydrogenation: $H_2$ = 60 mL/min, 1.0 MPa, 320 °C for 2.5 h (5 °C/min). The selectivity of CO is <5% during the hydrogenation.

**References:**

(1) C. Zhao,X. Chen, C. Zhao, *Energy Fuels* 2009, **23** , 4683-4687.

(2) Y. Han, C. Fang, X. Ji, J. Wei, Q. Ge, J. Sun, *ACS Catal.* 2020, **10**, 12098-12108.

(3) T. Numpilai, N. Chanlek, Y. Poo-Arporn, C. K. Cheng, N. Siri-Nguan,T. Sornchamni, M. Chareonpanich, P. Kongkachuichay, N. Yigit, G. Rupprechter, J. Limtrakul, T. Witoon *ChemCatChem* 2020, **12**, 3306-3320.

(4) J. V. Veselovskaya,A. I Lysikov, O. V. Netskina, D. V. Kuleshov, A. G. Okunev, *Ind. Eng. Chem. Res.* 2020, **59**, 7130-7139.

(5) J. V. Veselovskaya, V. S. Derevschikov,T. Y. Kardash, O. A. Stonkus,T. A. Trubitsina, A. G. Okunev, Int. J. Greenhouse Gas Control, 2013, **17**, 332-340.