Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supporting Information

Spatial analysis of CO_2 hydrogenation to higher hydrocarbons over alkali-metal promoted iron(II)oxalate-derived catalysts

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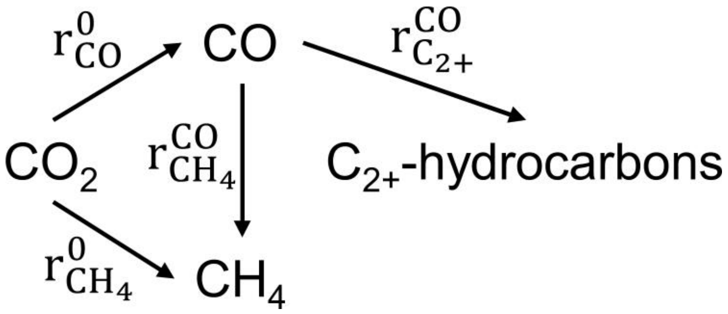
Supplementary note 1:

1.1 The approach for calculation of contribution of methane formation through CO or CO_2 hydrogenation into the overall methane production

There are two primary reactions in the course of CO_2-FTS: CO_2 conversion into CO through the reverse water gas shift reaction and CO_2 hydrogenation to CH_4. Hereafter, $r^0(CH_4)$ stands for the rate of CO_2 hydrogenation to CH_4 and $r^0(CO)$ is the rate of CO_2 conversion into CO. CO is further converted to CH_4 and C_{2+}-hydrocarbons. Thus, $r^{CO}(CH_4)$ is the abbreviation for the rate of CO hydrogenation into CH_4 and $r^{CO}(C_{2+})$ stands for the rate of CO hydrogenation into C_{2+}-hydrocarbons.



Scheme 1. A scheme showing overall pathways in the course of CO_2 conversion into various reaction products with the abbreviations used for the specific reaction rates.

As CO and CH_4 are the only products formed directly from CO_2, the primary (at zero level of CO_2 conversion) methane selectivity ($S^0(CH_4)$) can be expressed through $r^0(CO)$ and $r^0(CH_4)$ as reflected in equation S1. Using this expression, it is possible to estimate the ratio of $r^0(CO)$ to $r^0(CH_4)$ from $S^0(CH_4)$ (equation S2) and to obtain a relationship between $r^0(CO)$ and $r^0(CH_4)$ (equation S3).

$$S^0(CH_4) = \frac{r^0(CH_4)}{r^0(CH_4)+r^0(CO)} = \frac{1}{1+\frac{r^0(CO)}{r^0(CH_4)}} \qquad \text{(eq. S1)}$$

$$\frac{r^0(CO)}{r^0(CH_4)} = \frac{1-S^0(CH_4)}{S^0(CH_4)} \qquad \text{(eq. S2)}$$

$$r^0(CO) = \frac{1-S^0(CH_4)}{S^0(CH_4)} r^0(CH_4) \qquad \text{(eq. S3)}$$

The selectivity to methane at a non-zero level of CO_2 conversion ($S^i(CH_4)$) can be expressed by equation S4.

$$\mathrm{S^i(CH_4)} = \frac{\mathrm{r^0(CH_4)+r^{CO}(CH_4)}}{\mathrm{r^0(CO)-r^{CO}(C_{2+})-r^{CO}(CH_4)+r^{CO}(CH_4)+r^0(CH_4)+r^{CO}(C_{2+})}} = \frac{\mathrm{r^0(CH_4)+r^{CO}(CH_4)}}{\mathrm{r^0(CH_4)+r^0(CO)}} \quad \text{(eq. S4)}$$

Substituting the expression for $\mathrm{r^0(CO)}$ from equations S3 into equation S4 results in equation S5. The ratio of $\mathrm{r^{CO}(CH_4)}$ to $\mathrm{r^0(CH_4)}$ could be determined from the latter expression and is given in equation S6.

$$\mathrm{S^i(CH_4)} = \frac{\mathrm{r^0(CH_4)+r^{CO}(CH_4)}}{\mathrm{r^0(CH_4)}+\frac{\mathrm{1-S^0(CH_4)}}{\mathrm{S^0(CH_4)}}\mathrm{r^0(CH_4)}} = \frac{1+\frac{\mathrm{r^{CO}(CH_4)}}{\mathrm{r^0(CH_4)}}}{1+\frac{\mathrm{1-S^0(CH_4)}}{\mathrm{S^0(CH_4)}}} = \left(1+\frac{\mathrm{r^{CO}(CH_4)}}{\mathrm{r^0(CH_4)}}\right)\mathrm{S^0(CH_4)} \quad \text{(eq. S5)}$$

$$\frac{\mathrm{r^{CO}(CH_4)}}{\mathrm{r^0(CH_4)}} = \frac{\mathrm{S^i(CH_4)-S^0(CH_4)}}{\mathrm{S^0(CH_4)}} \quad \text{(eq. S6)}$$

As the total rate of $\mathrm{CH_4}$ production is defined as a sum of the reaction rates of $\mathrm{CH_4}$ formation through the primary and secondary pathways (equation S7), $\mathrm{r^0(CH_4)}$ and $\mathrm{r^{CO}(CH_4)}$ can be expressed by equations S8 and S9, respectively.

$$\mathrm{r^{total}(CH_4)} = \mathrm{r^0(CH_4)} + \mathrm{r^{CO}(CH_4)} \quad \text{(eq. S7)}$$

$$\mathrm{r^0(CH_4)} = \mathrm{r^{total}(CH_4)}\frac{\mathrm{S^0(CH_4)}}{\mathrm{S^i(CH_4)}} \quad \text{(eq. S8)}$$

$$\mathrm{r^{CO}(CH_4)} = \mathrm{r^{total}(CH_4)}\frac{\mathrm{S^i(CH_4)-S^0(CH_4)}}{\mathrm{S^i(CH_4)}} \quad \text{(eq. S9)}$$

Figures

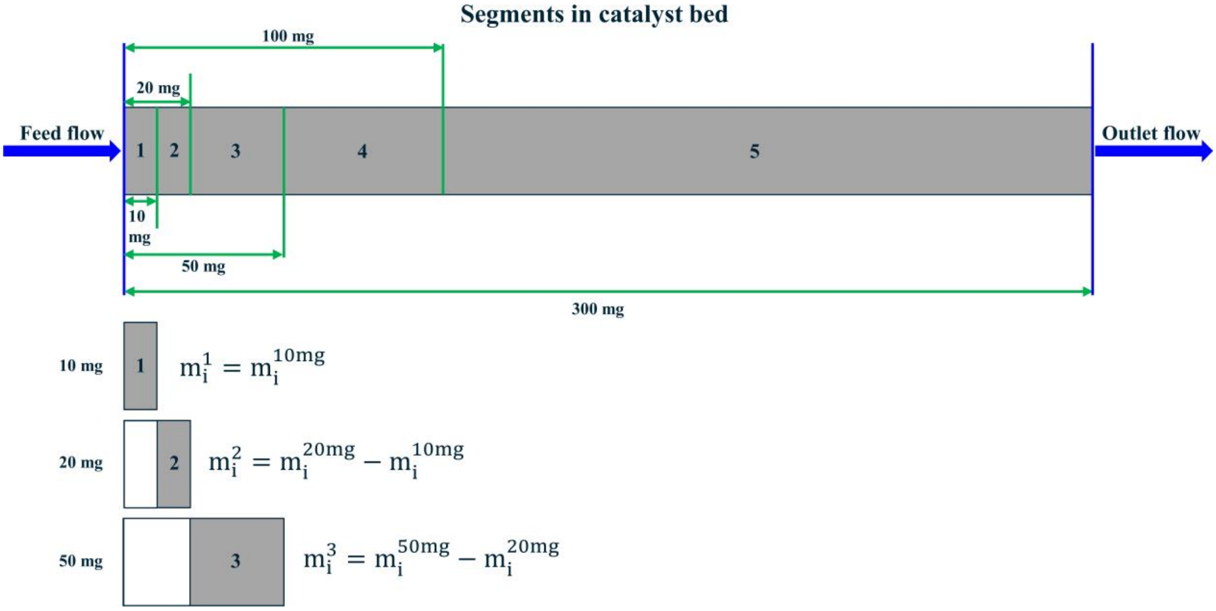


Fig. S 1. A schematic representation how the segments in the catalyst bed are defined.

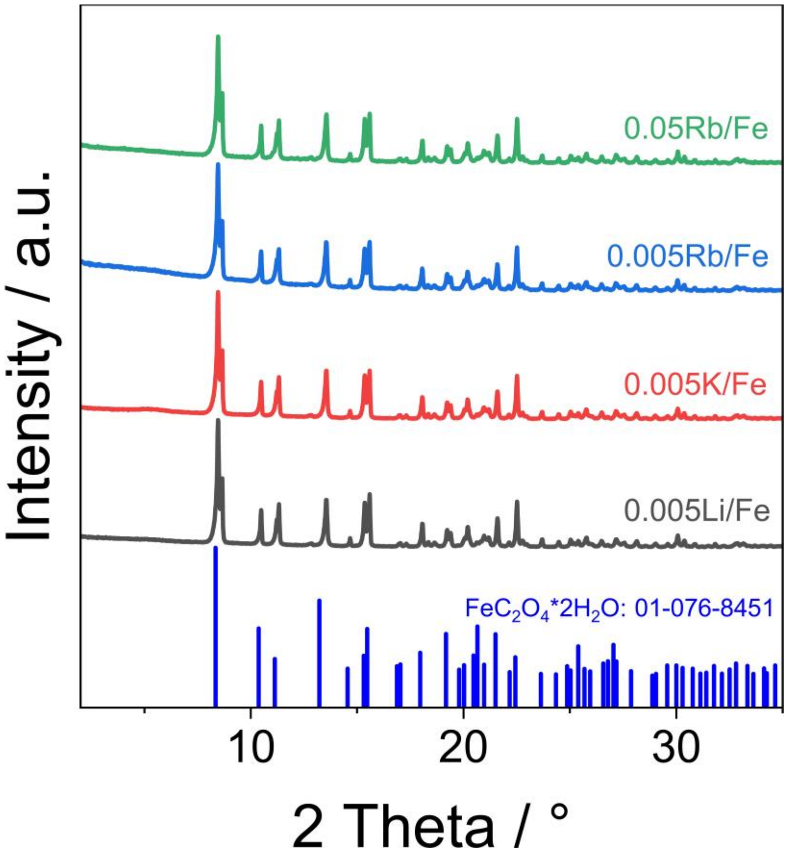


Fig. S 2. XRD patterns of iron (II) oxalate dihydrate and selected fresh catalysts with different alkali metals.

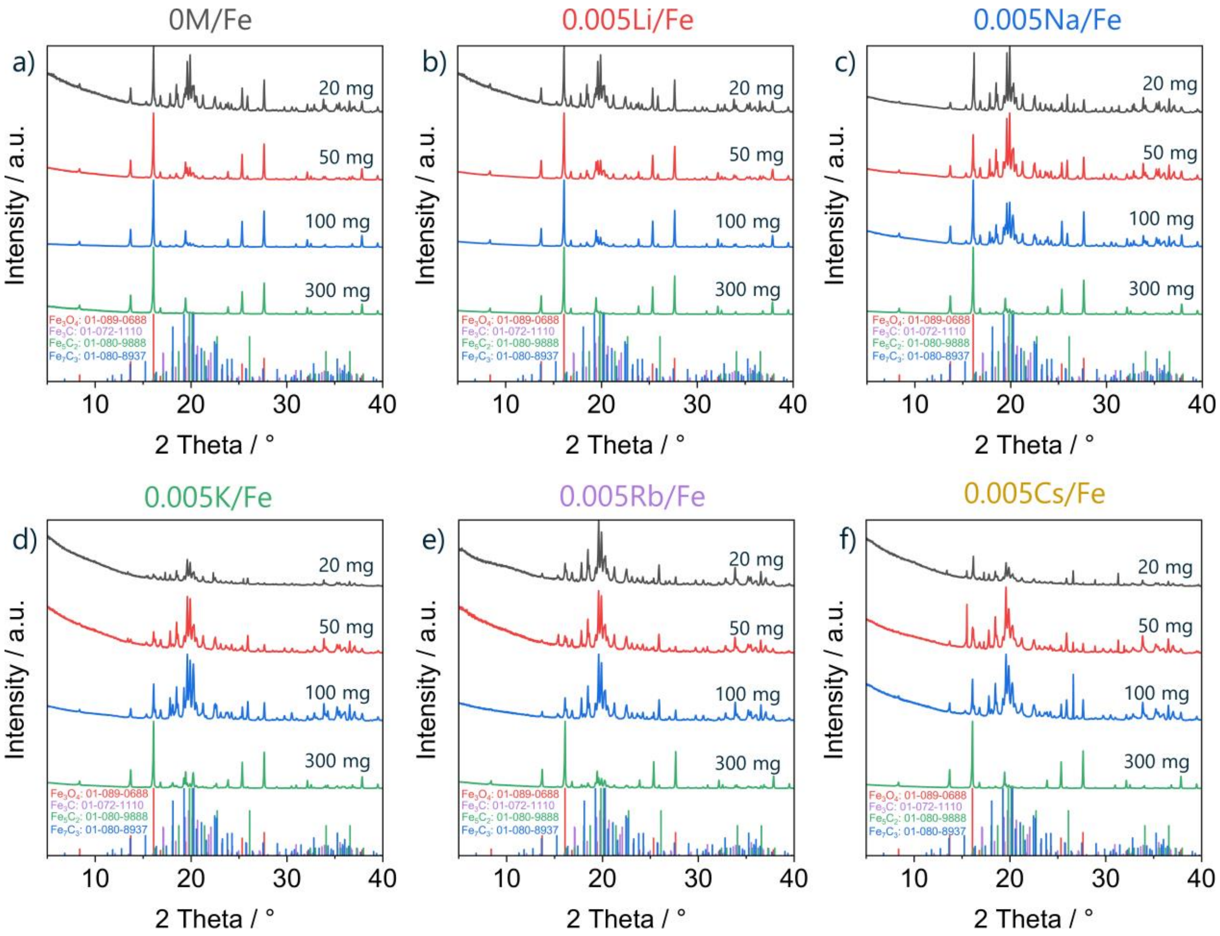


Fig. S 3. XRD patterns of spent (after CO_2 hydrogenation tests over 90 h on stream at 350 °C) catalysts with different alkali metals. The index lines characteristic for the crystalline phases present in the samples with the corresponding PDF numbers are also given as thin bars.

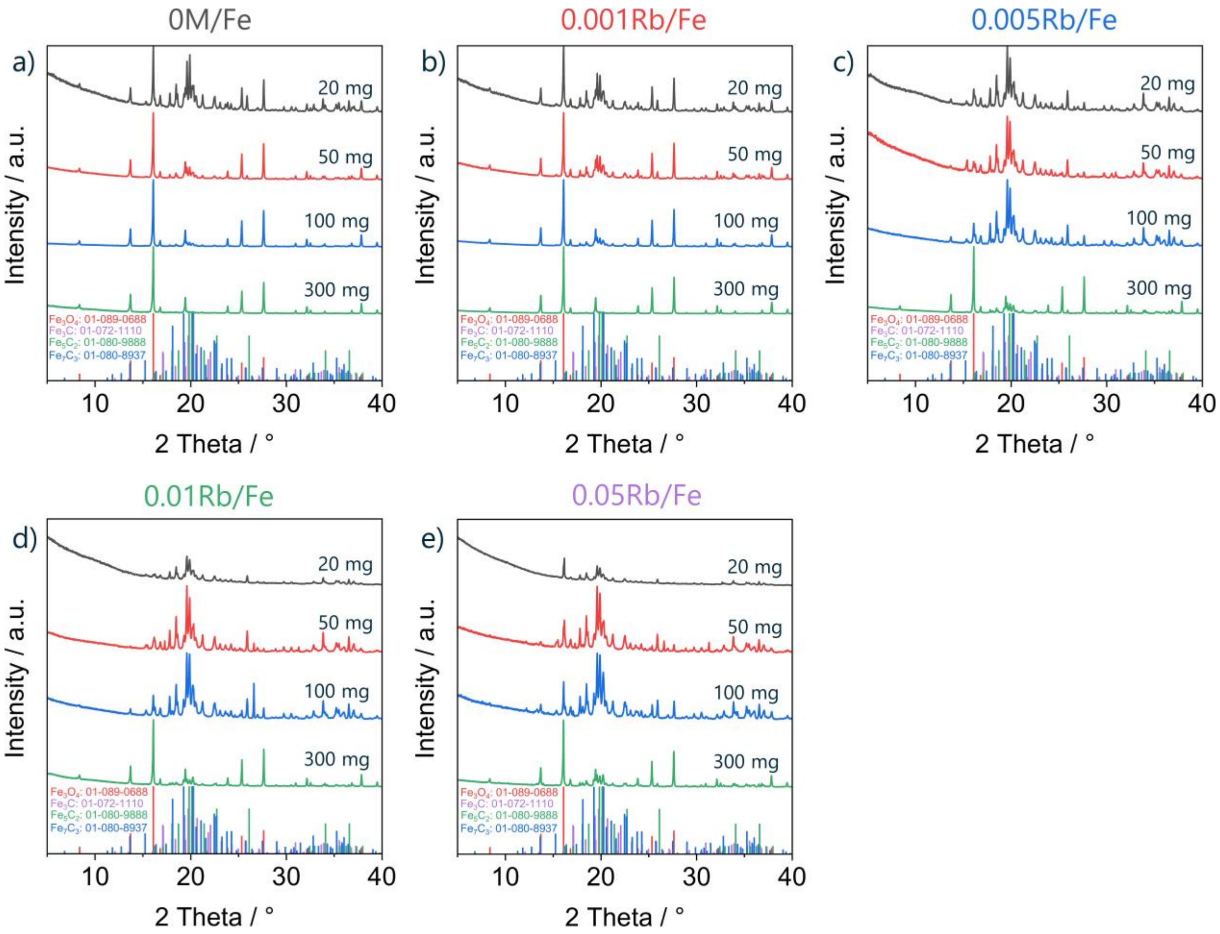


Fig. S 4. XRD patterns of spent (after CO_2 hydrogenation tests over 90 h on stream at 350 °C) catalysts containing different amounts of Rb. The index lines characteristic for the crystalline phases present in the samples with the corresponding PDF numbers are also given as thin bars.

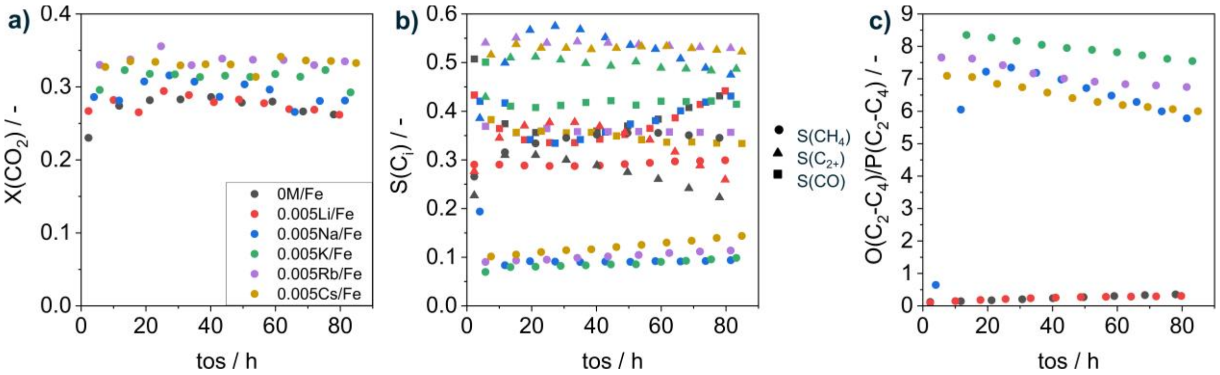


Fig. S 5. On-stream profiles of (a) CO_2 conversion, (b) product selectivity and (c) the olefin/paraffin ratio within C_2-C_4 hydrocarbons in CO_2 hydrogenation over catalysts promoted with different alkali metals. Reaction conditions: total pressure: 15 bar, reaction feed: CO_2:H_2:N_2 = 1:3:0.3, GHSV: 7020 mL/g_{cat}/h, temperature: 350 °C, catalyst amount: 50 mg.

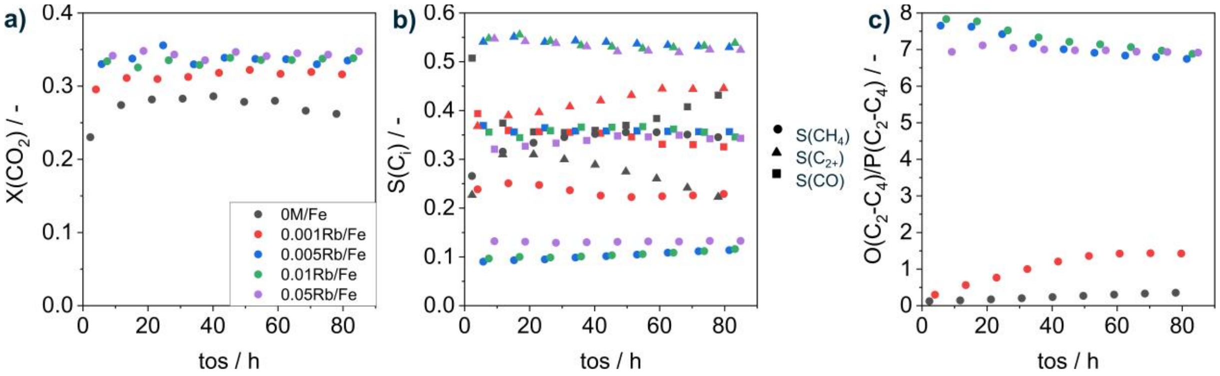


Fig. S 6. On-stream profiles of (a) CO_2 conversion, (b) product selectivity and (c) the olefin/paraffin ratio within C_2-C_4 hydrocarbons in CO_2 hydrogenation over catalysts promoted with different amounts of Rb. Reaction conditions: total pressure: 15 bar, reaction feed: CO_2:H_2:N_2 = 1:3:0.3, GHSV: 7020 mL/g_{cat}/h, temperature: 350 °C, catalyst amount: 50 mg.

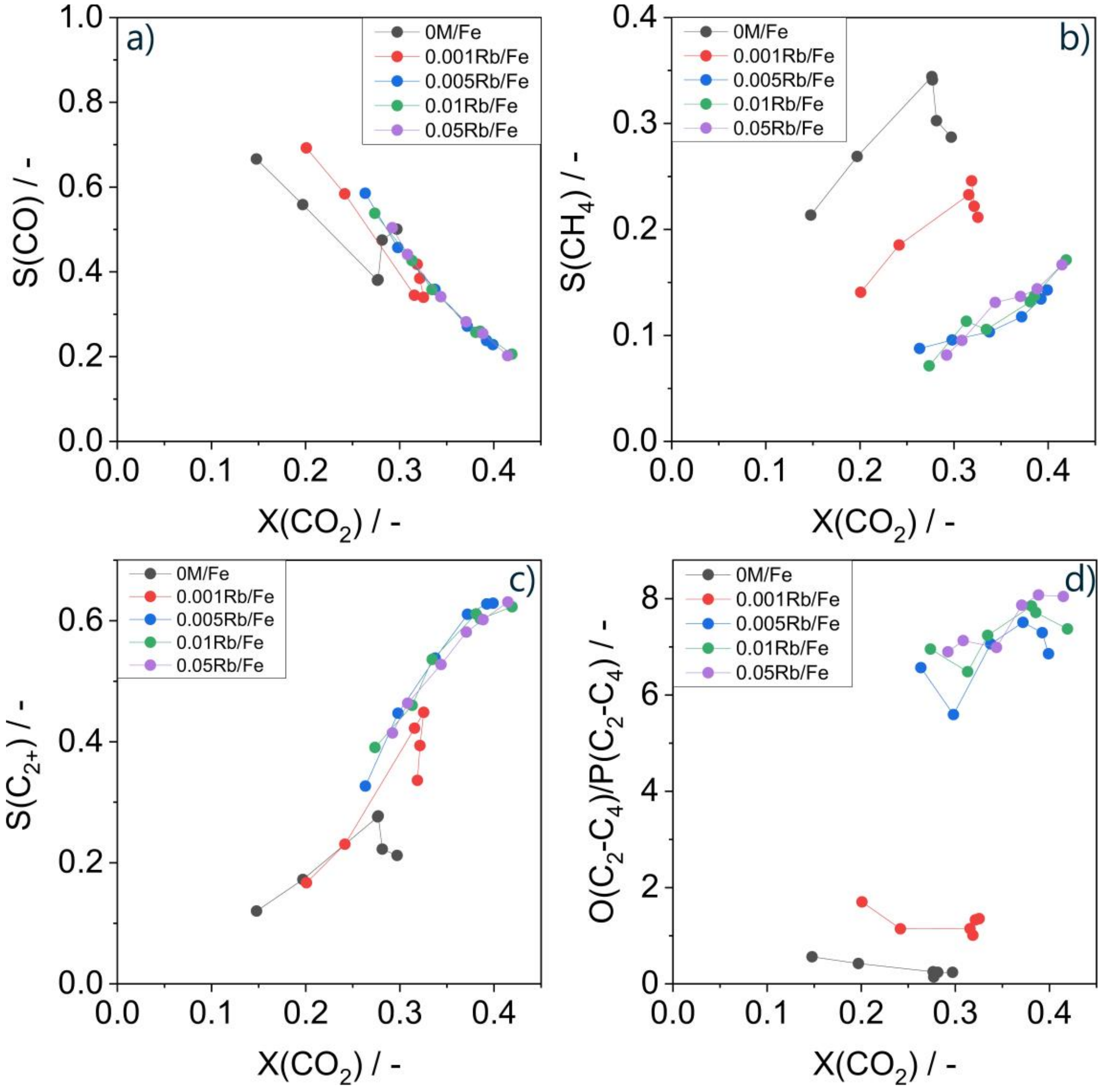


Fig. S 7. Selectivity-conversion relationships for (a) CO, (b) CH_4 and (c) C_{2+}-hydrocarbons as well as (d) the olefin/paraffin ratio within C_2-C_4 hydrocarbons dependence on CO_2 conversion obtained over catalysts promoted with different amounts of Rb. Reaction conditions: 350 °C, 15 bar, CO_2:H_2:N_2 = 1:3:0.3, GHSV: 585-35100 mL/g_{cat}/h.

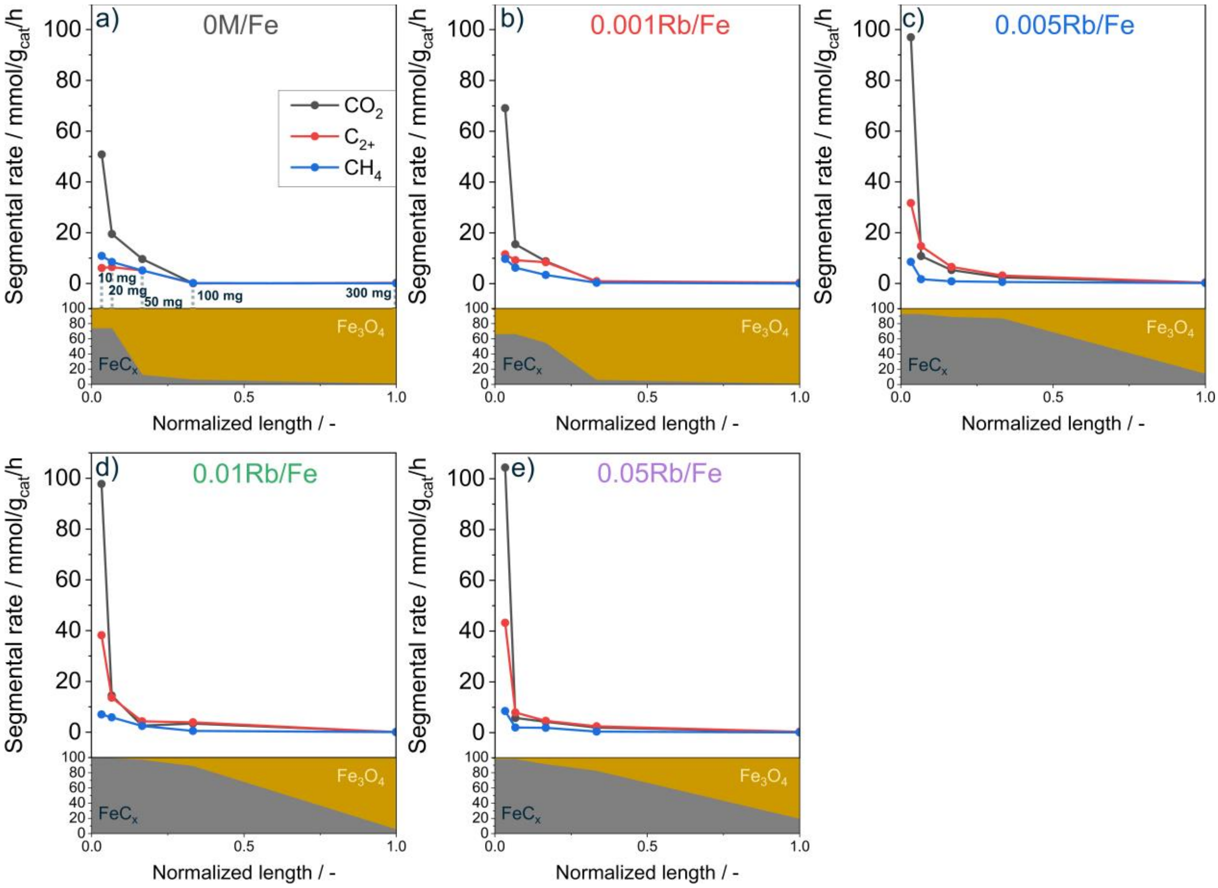


Fig. S 8. Spatial profiles of segmental overall CO_2 consumption rate, segmental CO_2 conversion rates to C_{2+}-hydrocarbons, or CH_4 determined over catalysts with different amounts of Rb promoter. Spatial distribution of iron phases along the catalyst bed is given in form of coloured areas. Fig. S1 shows how the segments are defined and how the rate values and the distribution profiles were calculated.

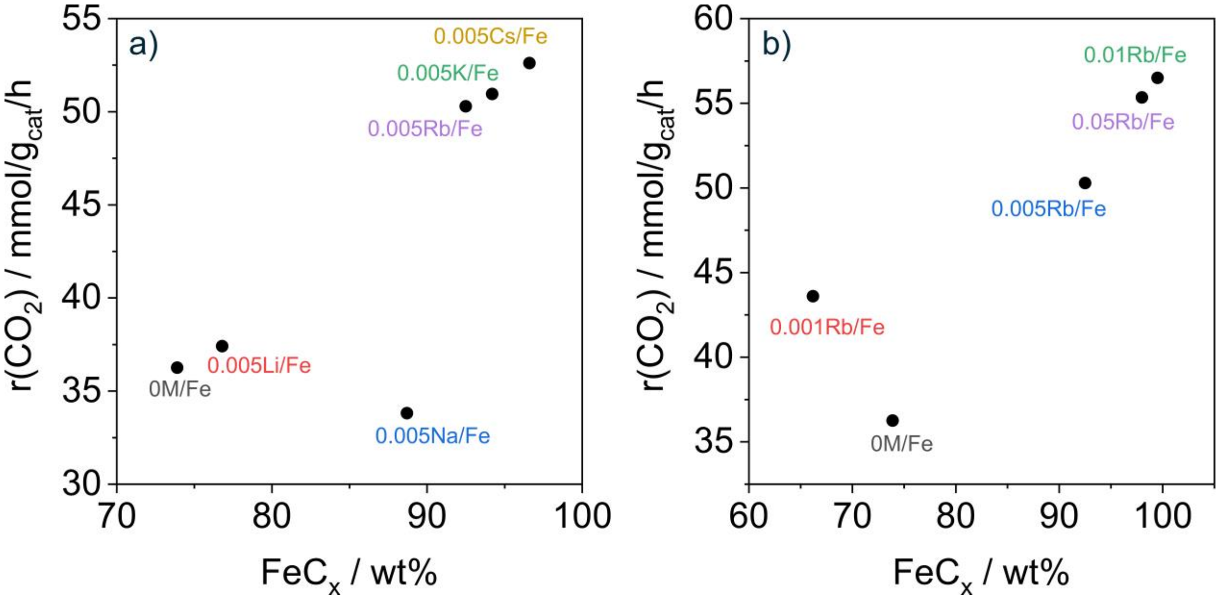


Fig. S 9. A correlation between the initial rate of CO_2 consumption (20 mg) and the fraction of iron carbides determined in 20 mg loading of spent catalysts promoted (a) with different alkali metals or (b) with different amounts of Rb.

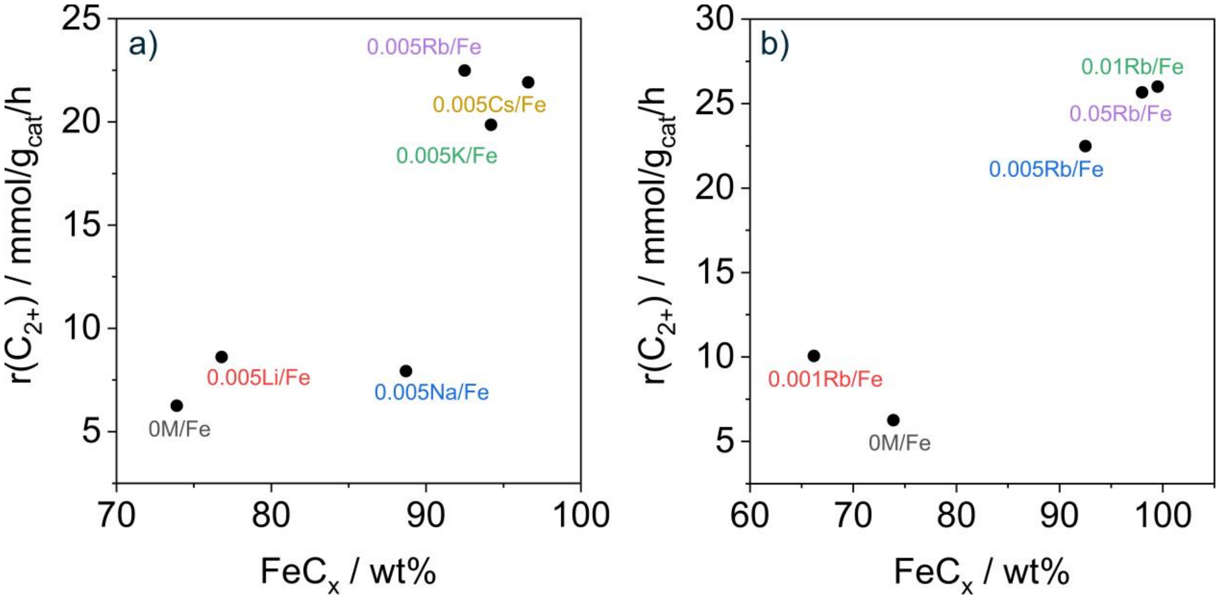


Fig. S 10. A correlation between the initial rate of C_{2+}-hydrocarbons formation (20 mg) and the fraction of iron carbide determined in 20 mg loading of spent catalysts promoted (a) with different alkali metals or (b) with different amounts of Rb.

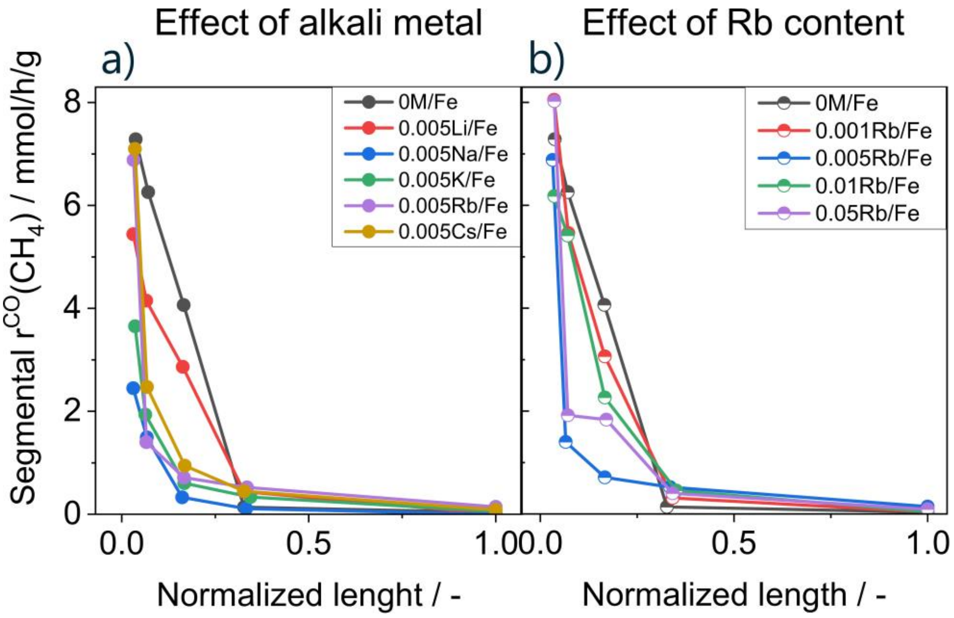


Fig. S 11. Spatial profiles of segmental rate of CO hydrogenation to CH_4 ($r^{CO}(CH_4)$) over catalysts (a) promoted with different alkali metals or (b) with different amounts of Rb. Fig. S1 shows how the segments are defined and how the rate values were calculated.

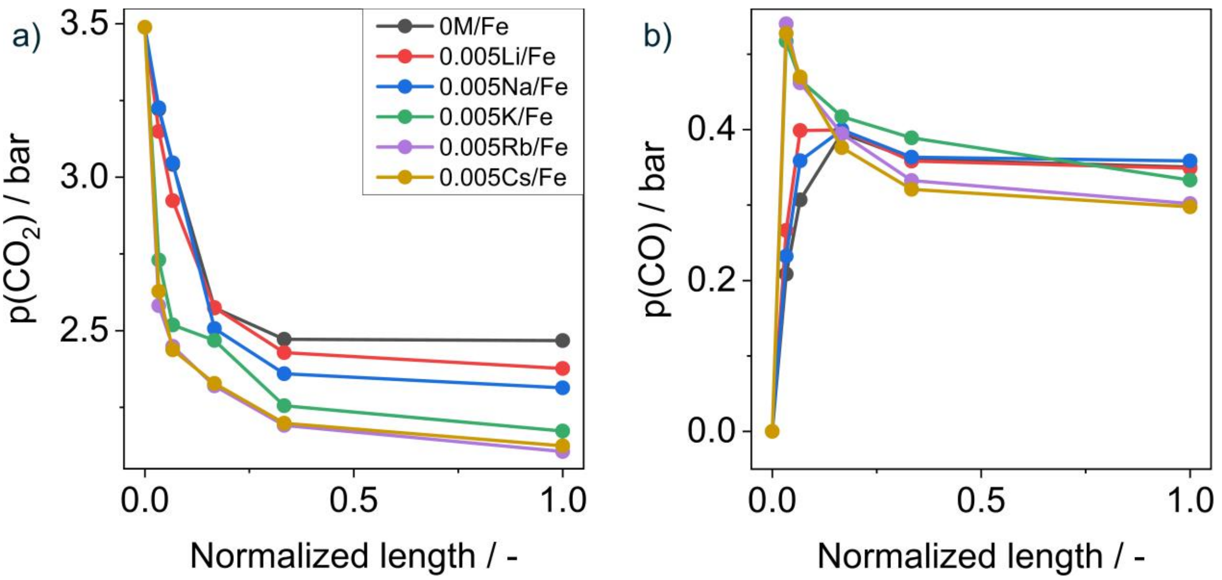


Fig. S 12. Partial pressure profiles of (a) CO_2 and (b) CO along the normalized catalyst bed length over catalysts promoted with different alkali metals.

Tables

Table S 1. The content of alkali metals determined by ICP or AAS (for Cs) analysis.

Catalyst	w(Fe) / %	w(M) / %	ν(Fe)[a] / mol	ν(M)[a] / mol	ν(M)/ν(Fe) / -
0.005Li/Fe	32.55	0.02	0.5828	0.0026	0.0045
0.005Na/Fe	32.18	0.07	0.5762	0.0032	0.0055
0.005K/Fe	32.53	0.08	0.5825	0.0021	0.0036
0.005Rb/Fe	32.17	0.24	0.5760	0.0028	0.0048
0.005Cs/Fe	32.20	0.29	0.5765	0.0022	0.0038
0.001Rb/Fe	74.01	0.11	1.3252	0.0013	0.0010
0.01Rb/Fe	72.83	1.21	1.3040	0.0142	0.0109
0.05Rb/Fe	66.05	5.00	1.1826	0.0585	0.0495

[a] *Calculated based on 100 g of a substance.*

Table S 2. Composition (wt%) of different loadings of spent catalysts (after 90 h on-stream) determined using Rietveld method for quantitative phase analysis.

Catalyst	Phase	Phase content in different catalyst amounts / %			
		20 mg	50 mg	100 mg	300 mg
0M/Fe	Fe_3O_4	26.1	63.0	78.4	92.3
	Fe_3C	8.6	4.8	2.7	0.9
	Fe_5C_2	65.3	32.2	18.9	6.8
	Fe_7C_3	0.0	0.0	0.0	0.0
0.005Li/Fe	Fe_3O_4	23.2	53.4	69.7	87.8
	Fe_3C	2.2	1.9	1.7	0.7
	Fe_5C_2	69.8	41.3	26.8	10.8
	Fe_7C_3	4.9	3.4	1.8	0.7
0.005Na/Fe	Fe_3O_4	11.3	19.0	30.0	74.0
	Fe_3C	2.0	1.6	1.3	0.6
	Fe_5C_2	79.4	72.3	61.9	22.2
	Fe_7C_3	7.2	7.1	6.8	3.2
0.005K/Fe	Fe_3O_4	5.8	7.7	16.0	71.0
	Fe_3C	0.0	0.0	0.0	0.0
	Fe_5C_2	84.9	83.3	76.0	26.0
	Fe_7C_3	9.3	9.0	8.0	3.0
0.005Rb/Fe	Fe_3O_4	7.5	9.7	11.4	61.2
	Fe_3C	4.4	3.4	2.5	1.5
	Fe_5C_2	84.6	83.6	83.1	36.3
	Fe_7C_3	3.5	3.3	3.0	1.0

Catalyst	Phase	20 mg	50 mg	100 mg	300 mg
0.005Cs/Fe	Fe_3O_4 / %	3.4	6.8	12.7	68.8
	Fe_3C / %	0.0	0.0	0.0	0.0
	Fe_5C_2 / %	87.7	86.4	81.6	28.5
	Fe_7C_3 / %	8.8	6.7	5.7	2.7
0.001Rb/Fe	Fe_3O_4 / %	33.8	40.8	67.5	88.8
	Fe_3C / %	8.9	4.9	3.0	1.0
	Fe_5C_2 / %	51.7	49.3	26.2	9.1
	Fe_7C_3 / %	5.5	5.0	3.3	1.1
0.01Rb/Fe	Fe_3O_4 / %	0.5	1.9	6.5	65.2
	Fe_3C / %	0.0	0.0	0.0	0.0
	Fe_5C_2 / %	90.2	90.2	86.8	32.4
	Fe_7C_3 / %	9.3	7.9	6.7	2.4
0.05Rb/Fe	Fe_3O_4 / %	2.0	6.0	11.7	57.7
	Fe_3C / %	0.0	0.0	0.0	0.0
	Fe_5C_2 / %	87.0	84.4	79.5	39.4
	Fe_7C_3 / %	11.0	9.6	8.8	2.9

Table S 3. Catalytic performance of the present and various state-of-art Fe-based promoted non-supported materials.

Catalyst	Promoter	AM/Fe / -	T / K	P / bar	GHSV / mL/g_{cat}/h	$X(CO_2)$ / %	$r(C_{2+})$ / mmol/g_{cat}/h	$r(C_2^=-C_4^=)$ / mmol/g_{cat}/h	Ref.
92.6Fe7.4K	K	0.114	573	25.0	560	41.7	2.1	0.5	1
92.6Fe7.4K	K	0.114	573	25.0	560	51.10	1.8	0.6	
92.6Fe7.4K	K	0.114	573	25.0	560	63.90	1.8	0.5	
88.3Fe7.1K4.6Co	K, Co	0.114	573	25.0	560	54.6	2.6	0.8	
84.0Fe6.7K9.3Co	K, Co	0.114	573	25.0	560	57.2	2.6	0.8	
10Fe0.8K	K	0.114	573	25.0	560	41.7	2.1	0.5	2
10Fe2.4K	K	0.343	573	25.0	560	37.8	1.9	0.4	
10Fe4.8K	K	0.685	573	25.0	560	35.2	1.8	0.3	
10Fe0.8K0.53Co	K, Co	0.115	573	25.0	560	54.6	2.6	0.8	
10Fe0.8K1.11Co	K, Co	0.114	573	25.0	560	57.2	2.6	0.8	
10Fe0.8K0.53Ru	K, Ru	0.114	573	25.0	560	47.1	2.3	0.6	
10Fe0.8K	K	0.114	533	25.0	560	30.0	1.6	0.2	
10Fe0.8K	K	0.114	593	25.0	560	42.6	2.1	0.5	
10Fe0.8K	K	0.114	613	25.0	560	49.5	2.4	0.6	
K-Fe15	K	0.020	543	5.0	2700	37.6	7.6	4.0	3
K-Fe15	K	0.020	573	5.0	2700	45.1	9.8	5.0	
K-Fe15	K	0.020	573	1.0	2700	24.2	0.2	0.1	

Catalyst	Promoter	AM/Fe / -	T / K	P / bar	GHSV / mL/g_{cat}/h	X(CO_2) / %	r(C_{2+}) / mmol/g_{cat}/h	r($C_2^=$-$C_4^=$) / mmol/g_{cat}/h	Ref.
K-Fe15	K	0.020	573	10.0	2700	48.5	10.9	5.1	
K-Fe15	K	0.020	573	5.0	5400	40.0	16.4	9.0	
K-Fe15	K	0.020	573	5.0	10800	38.0	29.8	16.3	
K-Fe15	K	0.020	573	5.0	16000	32.0	30.7	19.3	
Fe-Cu-Al-K	K, Cu, Al	0.086	573	10.0	1800	41.2	6.6	2.3	4
1K-Fe	K	0.014	613	20.0	1200	5.0	0.3	0.01	5
2K-Fe	K	0.029	613	20.0	1200	37.0	2.7	1.0	
5K-Fe	K	0.075	613	20.0	1200	38.0	2.8	1.2	
10K-Fe	K	0.159	613	20.0	1200	27.0	2.3	1.2	
16K-Fe	K	0.272	613	20.0	1200	25.0	2.0	0.9	
32K-Fe	K	0.672	613	20.0	1200	25.0	1.7	0.8	
5Li-Fe	Li	0.423	613	20.0	1200	27.0	1.7	0.7	
5Na-Fe	Na	0.128	613	20.0	1200	24.0	1.4	0.7	
5Rb-Fe	Rb	0.034	613	20.0	1200	42.0	2.9	1.5	
5Cs-Fe	Cs	0.022	613	20.0	1200	39.0	3.1	1.0	
0.5B-5K-Fe	K, B	0.076	613	20.0	1200	43.0	3.3	1.5	
1B-5K-Fe	K, B	0.076	613	20.0	1200	38.0	2.8	1.5	
3B-5K-Fe	K, B	0.078	613	20.0	1200	25.0	1.7	1.1	
5B-5K-Fe	K, B	0.079	613	20.0	1200	23.0	1.5	1.0	

Catalyst	Promoter	AM/Fe / -	T / K	P / bar	GHSV / mL/g_{cat}/h	X(CO_2) / %	r(C_{2+}) / mmol/g_{cat}/h	r($C_2^=$-$C_4^=$) / mmol/g_{cat}/h	Ref.
6B-5K-Fe	K, B	0.080	613	20.0	1200	22.0	1.3	0.7	
8B-5K-Fe	K, B	0.082	613	20.0	1200	21.0	1.0	0.4	
FeCu0.05Na0.07	Na, Cu	0.068	673	50.0	3000	41.0	8.6	-	6
FeCu0.01Na0.01	Na, Cu	0.014	673	50.0	3000	40.0	8.7	-	
Fe-Cu-Al-K	K, Cu, Al	0.086	548	10.0	500	39.8	1.9	0.7	7
Fe-Cu-Al-K	K, Cu, Al	0.086	573	10.0	2000	35.6	4.8	1.4	
Fe–Cu–K	K, Cu	0.057	538	12.5	2240	10.80	1.4	0.5	8
Fe–Cu–Al–K	K, Cu, Al	0.057	538	12.5	2240	11.30	1.3	0.4	
Fe–Cu–Si–K	K, Cu, Si	0.057	538	12.5	2240	10.20	0.9	0.1	
Fe–Cu–Al–K(2)	K, Cu, Al	0.057	538	12.5	2240	15.60	2.6	0.6	
Fe–Cu–Al–K(1)	K, Cu. Al	0.029	538	12.5	2240	13.20	1.8	0.2	
Fe–Cu–Al–K(2)	K, Cu, Al	0.057	538	12.5	2240	15.60	2.6	0.6	
Fe–Cu–Al–K(3)	K, Cu, Al	0.086	538	12.5	2240	16.90	3.1	0.7	
Fe–Cu–Al–K(4)	K, Cu, Al	0.114	538	12.5	2240	14.40	2.5	0.7	
Fe_3O_4-pur	Na	0.001	593	5.0	560	27.3	0.7	0.1	9
Fe_3O_4-EDA	Na	0.000	593	5.0	560	21.8	0.8	0.2	
Fe_3O_4-NaAc	Na	0.021	593	5.0	560	30.4	1.3	0.4	
Fe_3O_4-NaOH	Na	0.006	593	5.0	560	30.0	1.2	0.4	
0.025Na/Fe_3O_4-pur	Na	0.061	593	5.0	560	31.7	1.4	0.5	

Catalyst	Promoter	AM/Fe / -	T / K	P / bar	GHSV / mL/g_{cat}/h	X(CO_2) / %	r(C_{2+}) / mmol/g_{cat}/h	r($C_2^=$-$C_4^=$) / mmol/g_{cat}/h	Ref.
0.05Na/Fe_3O_4-pur	Na	0.121	593	5.0	560	29.6	1.2	0.5	
0.1Na/Fe_3O_4-pur	Na	0.243	593	5.0	560	29.5	1.2	0.4	
0.05K/Fe_3O_4-pur	K	0.071	593	5.0	560	33.0	1.5	0.4	
0.09Mn/Fe_3O_4-NaAc	Na, Mn	0.021	593	5.0	560	27.6	1.1	0.5	
0.04Mn/Fe_3O_4-NaAc	Na, Mn	0.021	593	5.0	560	27.9	1.1	0.4	
0.09Mn/Fe_3O_4-NaAc	Na, Mn	0.021	593	5.0	560	27.6	1.1	0.5	
0.14Mn/Fe_3O_4-NaAc	Na, Mn	0.021	593	5.0	560	27.0	1.0	0.5	
0.19Mn/Fe_3O_4-NaAc	Na, Mn	0.021	593	5.0	560	27.0	1.1	0.5	
0.01%Na/Fe_3O_4	Na	0.000	593	30.0	2040	26.8	3.5	-	10
0.05%Na/Fe_3O_4	Na	0.001	593	30.0	2040	32.5	5.1	-	
0.1%Na/Fe_3O_4	Na	0.002	593	30.0	2040	36.6	6.3	-	
0.5%Na/Fe_3O_4	Na	0.012	593	30.0	2040	38.4	6.7	-	
1%Na/Fe_3O_4	Na	0.024	593	30.0	2040	37.2	6.5	-	
3%Na/Fe_3O_4	Na	0.073	593	30.0	2040	36.8	6.4	-	
5%Na/Fe_3O_4	Na	0.121	593	30.0	2040	36.5	6.3	-	
FeNa(0.08)	Na	0.002	593	30.0	2000	35.7	5.1	1.5	11
FeNa(0.16)	Na	0.004	593	30.0	2000	38.4	6.0	3.0	
FeNa(0.43)	Na	0.010	593	30.0	2000	39.6	6.2	3.3	
FeNa(1.18)	Na	0.029	593	30.0	2000	40.5	6.3	3.5	

Catalyst	Promoter	AM/Fe / -	T / K	P / bar	GHSV / mL/g_{cat}/h	$X(CO_2)$ / %	$r(C_{2+})$ / mmol/g_{cat}/h	$r(C_2^=-C_4^=)$ / mmol/g_{cat}/h	Ref.
FeNa(7.03)	Na	0.171	593	30.0	2000	40.0	6.1	3.4	12
1Na/Fe	Na	0.024	593	30.0	2040	36.8	6.4	1.8	
0.1Mn–Na/Fe	Na, Mn	0.024	593	30.0	2040	35.7	6.1	1.8	
1Mn–Na/Fe	Na, Mn	0.024	593	30.0	2040	39.3	6.8	2.1	
5Mn–Na/Fe	Na, Mn	0.024	593	30.0	2040	38.6	6.2	2.4	
10Mn–Na/Fe	Na, Mn	0.024	593	30.0	2040	37.7	5.8	2.3	
Fe–K	K	0.100	593	20.0	1000	48.3	4.0	2.4	13
7Fe–1Zr–K	K, Zr	0.100	593	20.0	1000	49.8	4.1	2.7	
5Fe–1Zr–K	K, Zr	0.100	593	20.0	1000	54.4	4.7	3.1	
3Fe–1Zr–K	K, Zr	0.100	593	20.0	1000	51.6	4.1	2.6	
1Fe–1Zr–K	K, Zr	0.100	593	20.0	1000	43.4	3.3	2.0	
5Fe–1Zr–K[C]	K, Zr	0.100	593	20.0	1000	34.0	2.9	1.8	
Fe-2.44Na	Na	0.091	593	30.0	4000	34.5	11.2	3.7	14
$ZnFeO_x$-0.50Na	Na, Zn	0.023	593	30.0	4000	28.6	6.9	0.3	
$ZnFeO_x$-2.68Na	Na, Zn	0.127	593	30.0	4000	38.6	12.4	4.5	
$ZnFeO_x$-4.25Na	Na, Zn	0.207	593	30.0	4000	38.4	12.4	4.8	
$ZnFeO_x$-5.79Na	Na, Zn	0.289	593	30.0	4000	33.8	11.0	3.4	
$ZnFeO_x$-20.00Na	Na, Zn	1.263	593	30.0	4000	29.3	9.1	2.8	
1%Na-50Co50Fe	Na, Co	0.048	493	9.2	2000	7.3	0.2	-	15

Catalyst	Promoter	AM/Fe / -	T / K	P / bar	GHSV / mL/g_{cat}/h	$X(CO_2)$ / %	$r(C_{2+})$ / mmol/g_{cat}/h	$r(C_2^=-C_4^=)$ / mmol/g_{cat}/h	Ref.
1%Na-50Co50Fe	Na, Co	0.048	543	9.2	2000	22.7	1.0	-	
1.7%K-50Co50Fe	K, Co	0.050	493	9.2	2000	10.3	0.1	-	
1.7%K-50Co50Fe	K, Co	0.050	543	9.2	2000	22.6	0.7	-	
95Fe-K	K, Mn	0.005	573	10.1	8280	9.9	3.5	-	16
95Fe-Na	Na, Mn	0.014	573	10.1	8280	10.9	1.7	-	
95Fe-CuK	K, Cu, Mn	0.009	573	10.1	8280	21.8	9.2	-	
Na-Fe_3O_4	Na	0.176	593	30.0	8000	34.0	21.0	-	17
0.005Li/Fe	Li	0.005	623	15.0	12600	27.6	12.2	1.8	Present work
0.005Li/Fe	Li	0.005	623	15.0	6300	29.9	7.2	1.0	Present work
0.005Na/Fe	Na	0.005	623	15.0	12600	29.2	19.9	9.4	Present work
0.005Na/Fe	Na	0.005	623	15.0	6300	31.3	11.2	5.2	Present work
0.005K/Fe	K	0.005	623	15.0	63200	22.5	40.5	17.3	Present work
0.005K/Fe	K	0.005	623	15.0	6300	34.6	12.4	6.1	Present work

Catalyst	Promoter	AM/Fe / -	T / K	P / bar	GHSV / mL/g_{cat}/h	$X(CO_2)$ / %	$r(C_{2+})$ / mmol/g_{cat}/h	$r(C_2^=-C_4^=)$ / mmol/g_{cat}/h	Ref.
0.005Rb/Fe	Rb	0.005	623	15.0	63200	26.3	57.0	26.9	Present work
0.005Rb/Fe	Rb	0.005	623	15.0	6300	37.2	14.6	7.2	Present work
0.005Cs/Fe	Cs	0.005	623	15.0	63200	24.6	46.6	25.2	Present work
0.005Cs/Fe	Cs	0.005	623	15.0	6300	35.9	13.8	6.7	Present work
0.05Rb/Fe	Rb	0.05	623	15.0	63200	29.2	77.9	32.0	Present Work
0.05Rb/Fe	Rb	0.05	623	15.0	6300	37.1	14.2	7.4	Present work

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