Supporting Information

Promotional Effects on the Catalytic Activity of Co-Fe Alloy Supported on Graphitic Carbon for CO_2 Hydrogenation

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Sample characterization

Field Emission scanning electron microscopy (FESEM) images were acquired by using a JEOL JSM 6300 apparatus. HRTEM images were recorded in a JEOL JEM 2100F under an accelerating voltage of 200 kV. Samples were prepared by applying one drop of the suspended material in ethanol onto a carbon-coated nickel TEM grid and allowing them to dry at room temperature. Raman spectra were collected with a Horiba Jobin Yvon-Labram HR UV-visible-NIR (200-1600 nm) Raman Microscope Spectrometer using a 512 nm laser. The chemical composition of the samples was determined by combustion chemical analysis by using a CHNS FISONS elemental analyser.

Catalytic Tests

A setup (Microactivity tester, PID Eng&Tech) equipped with a stainless steel (316 SS) fixed bed tube reactor (Autoclave Engineers) featured with an inner K-type thermocouple was used. Two mass flow controllers (EL-FLOW Select, Bronkhorst) were used to feed the mixture of the inlet gases: hydrogen (5.0, Linde) and carbon dioxide (4.5, Linde). The total gas flow rate was checked before each experiment using a gas calibrated burette connected to the outlet of the reactor setup. After catalyst activation at 300 ^{o}C under N_2, an amount of 40 mg catalyst powder was introduced in the reactor. Air was removed by flushing the system at room temperature for 15 min with 30 mL/min H_2 and 10 mL/min CO_2, followed by 30 min catalytic reaction at the flow rates of different ratio of H_2 and CO_2 (in total 4 mL/min). Afterwards, the reactor was pressurized at 10 bar depending on different reactions. Each sample was submitted to a 5 h test starting at 250 ^{o}C and increasing the temperature in 50 ^{o}C steps. Each temperature was maintained for 1 h period before increasing another 50 ^{o}C. Analysis of the reaction products was carried out on line with multichannel gas chromatography that quantifies the percentage of CO_2, CO, CH_4 and C_{2+} products. Data at each temperature corresponds to the average value of the analysis measured for each temperature at 30, 45 and 55 min after the stabilization of the temperature. The values of the CO_2 conversion obtained from the GC measurements coincided very well in all the experiments, indicating that the reactor setup reached the steady state operation conditions.

GC analyses were performed using H_2 as carrier gas on an Agilent 7890A chromatograph equipped with a capillary PLOT column (RT-Msieve 5A, Restek) and a thermal conductivity detector (TCD). Oven temperature program started with a 5 min dwell at 50 ^{o}C, then continue with a ramp with 25 ^{o}C/min up to 250 ^{o}C followed by a final dwell of

5 min, allowing thus a very good separation between CH_4, CO and CO_2. The gas samples were injected through a remotely controlled 6-way valve (A4C6WE, Vici) kept at ambient temperature. The reproducibility of the analysis system was checked prior to each experiment by injecting a series of three successive samples of standard gas mixtures of known composition passed through the reactor at room temperature.

Table S1. List of samples under study.

Sample No.	Metal source	m (mg)	Thiourea (mg/mL)
1	$CoCl_2$	146.5	-
	$FeCl_2$	38.9	
2	$CoCl_2$	146.5	-
	$FeCl_2$	38.9	
	$PdCl_2$	7.5	
3	$Co(OAc)_2$	150	-
	$Fe(OAc)_2$	50	
4	$Co(OAc)_2$	150	-
	$Fe(OAc)_2$	50	
	$Ce(OAc)_3{\cdot}xH_2O$	10	
5	$CoCl_2{\cdot}6H_2O$	150	-
	$FeCl_2$	75	
6	$Co(OAc)_2$	240	-
	$Fe(OAc)_2$	100	
7	$CoCl_2{\cdot}6H_2O$	951.7	-
	$FeCl_2$	101.4	
	$Ce(OAc)_3{\cdot}xH_2O$	126.9	
8	$CoCl_2$	146.5	20
	$FeCl_2$	38.9	
9	$CoCl_2$	146.5	5
	$FeCl_2$	38.9	
10	$CoCl_2$	146.5	2
	$FeCl_2$	38.9	
11	$Co(OAc)_2$	40	2
	$Fe(OAc)_2$	16.5	
	NaOAc	8	
	KOAc	4	

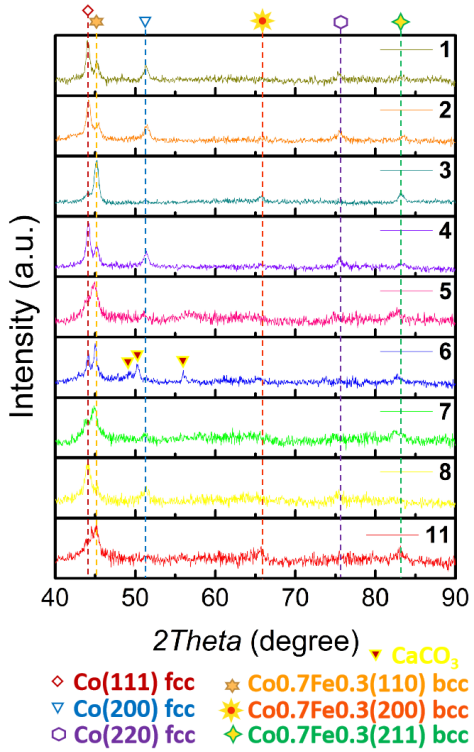

Figure S1. XRD patterns of the samples **1**-**11**.

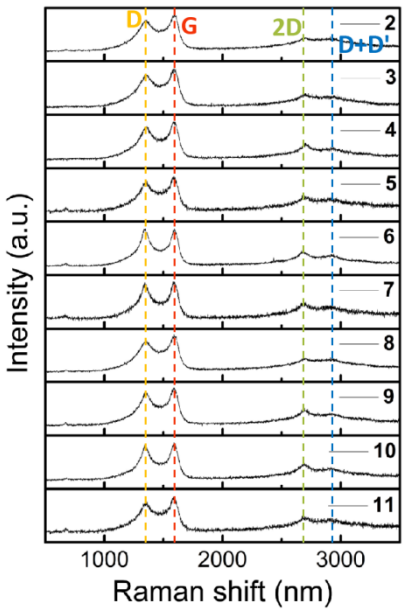

Figure S2. Rraman spectrums of the samples 2-11.

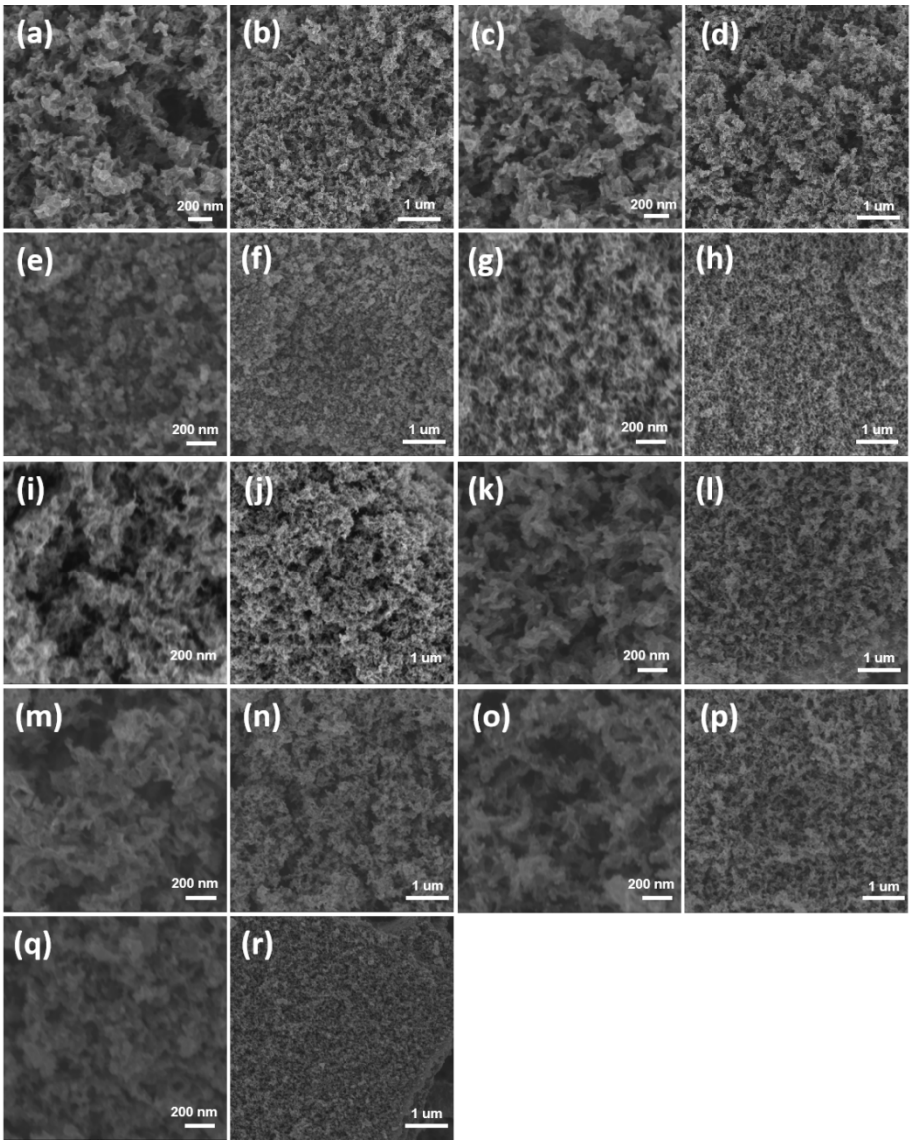

Figure S3. FESEM images of samples **2**-**5**, **7**-**11**. (**a**, **b**: sample **2**; **c**, **d**: sample **3**; **e**, **f**: sample **4**; **g**, **h**: sample **5**; **i**, **j**: sample **7**; **k**, **l**: sample **8**; **m**, **n**: sample **9**; **o**, **p**: sample **10**; **q**, **r**: sample **11**.).

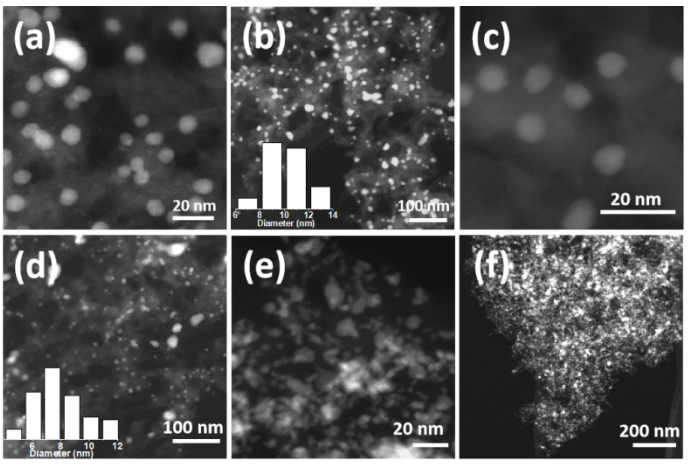

Figure S4. DF-TEM images of samples **1**, **3** and **7**. (**a**, **b**: sample **1**; **c**, **d**: sample **3**; **e**, **f**: sample **7**.).

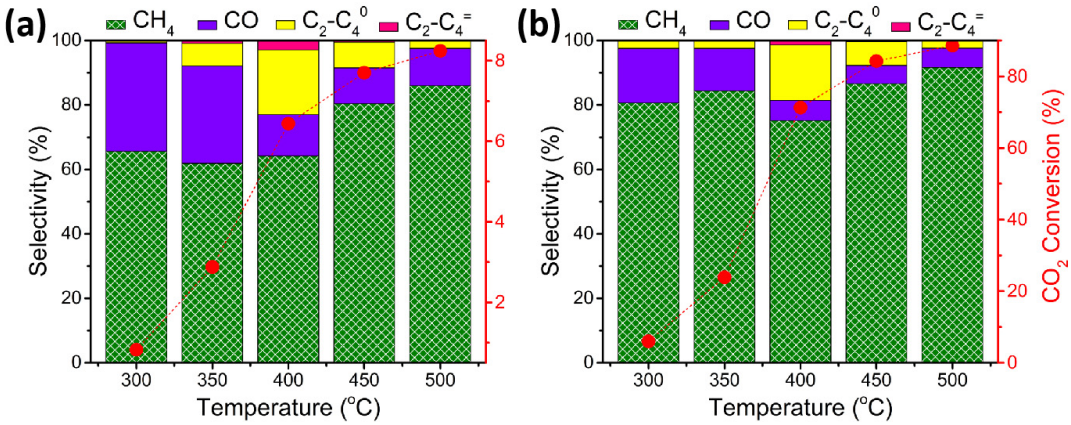

Figure S5. CO_2 conversion and selectivity for samples **3** and **4** at different temperature. (**a**: sample **3** and **b**: sample **4**. Reaction condition: H_2/CO_2 ratio of 7, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

Table S2. CO_2 conversion and selectivity for sample **1** on different temperature. (Reaction condition: H_2/CO_2 ratio of 7, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
300	9.8	81.3	1.3	0	0	0	0	17.4	1.3	0	1.3
350	32.7	76.1	4.4	1.6	1.4	0	0.5	16.0	7.4	0.5	7.9
400	74.4	68.4	11.9	7.4	3.5	0.6	1.4	6.9	22.8	2.0	24.8
450	82.9	83.0	6.9	1.8	0.6	0.3	0.3	7.2	9.3	0.5	9.8
500	87.9	91.4	2.1	0.2	0	0.1	0	6.3	2.3	0.1	2.3

Table S3. CO_2 conversion and selectivity for sample **2** on different temperature. (Reaction condition: H_2/CO_2 ratio of 7, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
300	19.6	68.0	6.1	2.8	3.2	0	2.1	17.9	12.1	2.1	14.1
350	39.6	84.4	2.4	2.3	1.6	0	0.8	8.5	6.3	0.8	7.1
400	74.4	85.1	6.6	2.0	0.9	0	0.4	5.1	9.4	0.4	9.8
450	83.8	89.7	4.0	0.5	0	0.1	0.1	5.5	4.6	0.3	4.8
500	84.7	91.4	1.5	0.2	0	0	0	6.9	1.7	0	1.7

Table S4. CO_2 conversion and selectivity for sample **3** on different temperature. (Reaction condition: H_2/CO_2 ratio of 7, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
300	8.2	65.6	0.7	0	0	0	0	33.7	0.7	0	0.7
350	28.8	61.9	3.8	1.6	1.6	0	0.9	30.3	7.0	0.9	7.9
400	64.4	64.2	11.4	5.3	3.4	0.8	2.1	12.8	20.1	2.9	23.0
450	77.0	80.3	6.3	1.3	0.4	0.2	0.3	11.2	8.0	0.5	8.5
500	82.4	86.0	2.2	0.2	0	0	0	11.6	2.4	0	2.4

Table S5. CO_2 conversion and selectivity for sample **4** on different temperature. (Reaction condition: H_2/CO_2 ratio of 7, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
300	6.0	80.6	2.5	0	0	0	0	16.9	2.5	0	2.5
350	23.9	84.4	2.4	0	0	0	0	13.2	2.4	0	2.4
400	71.3	75.2	9.8	5.2	2.2	0.3	1.1	6.2	17.2	1.4	18.6
450	84.3	86.6	5.8	1.3	0.3	0.2	0.2	5.6	7.4	0.4	7.8
500	88.6	91.6	2.2	0.3	0	0	0	6.0	2.4	0	2.4

Table S6. CO_2 conversion and selectivity for sample **5** on different temperature. (Reaction condition: H_2/CO_2 ratio of 7, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
250	6.8	86.0	3.0	7.6	0	0	0	3.4	10.6	0	10.6
300	24.5	92.0	3.6	1.5	0	0	0	2.9	5.1	0	5.1
350	50.9	88.4	6.6	2.0	0.8	0	0	2.3	9.3	0	9.3
400	72.2	90.2	6.2	1.1	0.3	0	0	2.2	7.5	0	7.5
450	80	94.5	2.7	0.1	0	0	0	2.7	2.8	0	2.8

Table S7. CO_2 conversion and selectivity for sample **6** on different temperature. (Reaction condition: H_2/CO_2 ratio of 7, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
300	32.1	95.8	1.8	0.8	0	0	0	1.7	2.5	0	2.5
350	65.6	95.9	2.3	0.3	0	0	0	1.5	2.6	0	2.6
400	84.8	96.9	1.6	0.1	0	0	0	1.4	1.7	0	1.7
450	92.1	97.9	0.8	0.1	0	0	0	1.2	0.9	0	0.9

500	94.2	97.8	0.6	0.1	0	0	0	1.5	0.7	0	0.7

Table S8. CO_2 conversion and selectivity for sample **7** on different temperature. (Reaction condition: H_2/CO_2 ratio of 4, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
250	1.4	41.4	16.0	17.8	0	0	0	24.8	33.8	0	33.8
300	4.8	54.4	3.7	8.8	0	0	0	33.1	12.5	0	12.5
350	12.3	49.9	5.3	2.2	2.7	0	0	39.8	10.3	0	10.3
400	37.3	61.3	10.5	5.1	1.9	0	0.3	20.9	17.5	0.3	17.8
450	62.0	79.2	7.6	1.4	0.2	0	0.1	11.5	9.1	0.1	9.2

Table S9. CO_2 conversion and selectivity for sample **8** on different temperature. (Reaction condition: H_2/CO_2 ratio of 3, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
300	1.6	0	14.4	48.1	0	0	30.7	6.9	62.5	30.7	93.1
350	0.5	0	9.2	0	0	0	0	90.8	9.2	0	9.2
400	1.8	0	2.7	0	0	0	0	97.3	2.7	0	2.7
450	6.7	1.6	0.8	0	0	0	0	97.7	0.8	0	0.8
500	19.6	1.5	0.6	0	0	0	0	98.0	0.6	0	0.6

Table S10. CO_2 conversion and selectivity for sample **9** on different temperature. (Reaction condition: H_2/CO_2 ratio of 2, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
300	1.4	0	19.8	40.9	0	0	21.9	17.4	60.7	21.9	82.7
350	1.0	0	6.2	0	0	0	0	93.8	6.2	0	6.2
400	3.7	2.1	1.1	0	0	0	0	96.9	1.1	0	1.1
450	11.4	1.1	0.5	0	0	0	0	98.4	0.5	0	0.5
500	31.1	1.2	0.4	0	0	0	0	98.4	0.4	0	0.4

Table S11. CO_2 conversion and selectivity for sample **10** on different temperature. (Reaction condition: H_2/CO_2 ratio of 1, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
300	1.0	0	23.3	38.7	0	0	23.5	14.5	62.0	23.5	85.5
350	0.7	0	5.6	0	0	0	0	94.4	5.6	0	5.6
400	2.0	4.2	2.6	0	0	0	0	93.2	2.6	0	2.6
450	5.1	2.3	1.2	0	0	0	0	96.5	1.2	0	1.2
500	13.2	1.7	1.2	0	0	0	0	97.1	1.2	0	1.2

Table S12. CO_2 conversion and selectivity for sample **11** on different temperature. (Reaction condition: H_2/CO_2 ratio of 1, total flow 4 mL/min, 10 bar, 40 mg catalyst.).

T (°C)	C (%) CO_2	S (%) CH_4	S (%) C_2H_6	S (%) C_3H_8	S (%) *n*-C_4H_{10}	S (%) C_2H_4	S (%) C_3H_6	S (%) CO	S (%) C_2-C_4^0	S (%) C_2-$C_4^=$	S (%) C_2-C_4
300	4.3	1.8	3.4	0	0	0	5.9	88.9	3.4	5.9	9.3
350	15.3	0.6	0.9	0	0	0	0	98.5	0.9	0	0.9
400	30.6	0.6	0.3	0	0	0	0	99.1	0.3	0	0.3
450	46.2	0.7	0.2	0	0	0	0	99.1	0.2	0	0.2
500	59.2	1.2	0.5	0	0	0	0	98.3	0.5	0	0.5