CO2 conversion into hydrocarbons via modified Fischer-Tropsch synthesis by using bulk iron catalysts combined with zeolites

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Supporting Information

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1.1 N_2 physisorption measurements

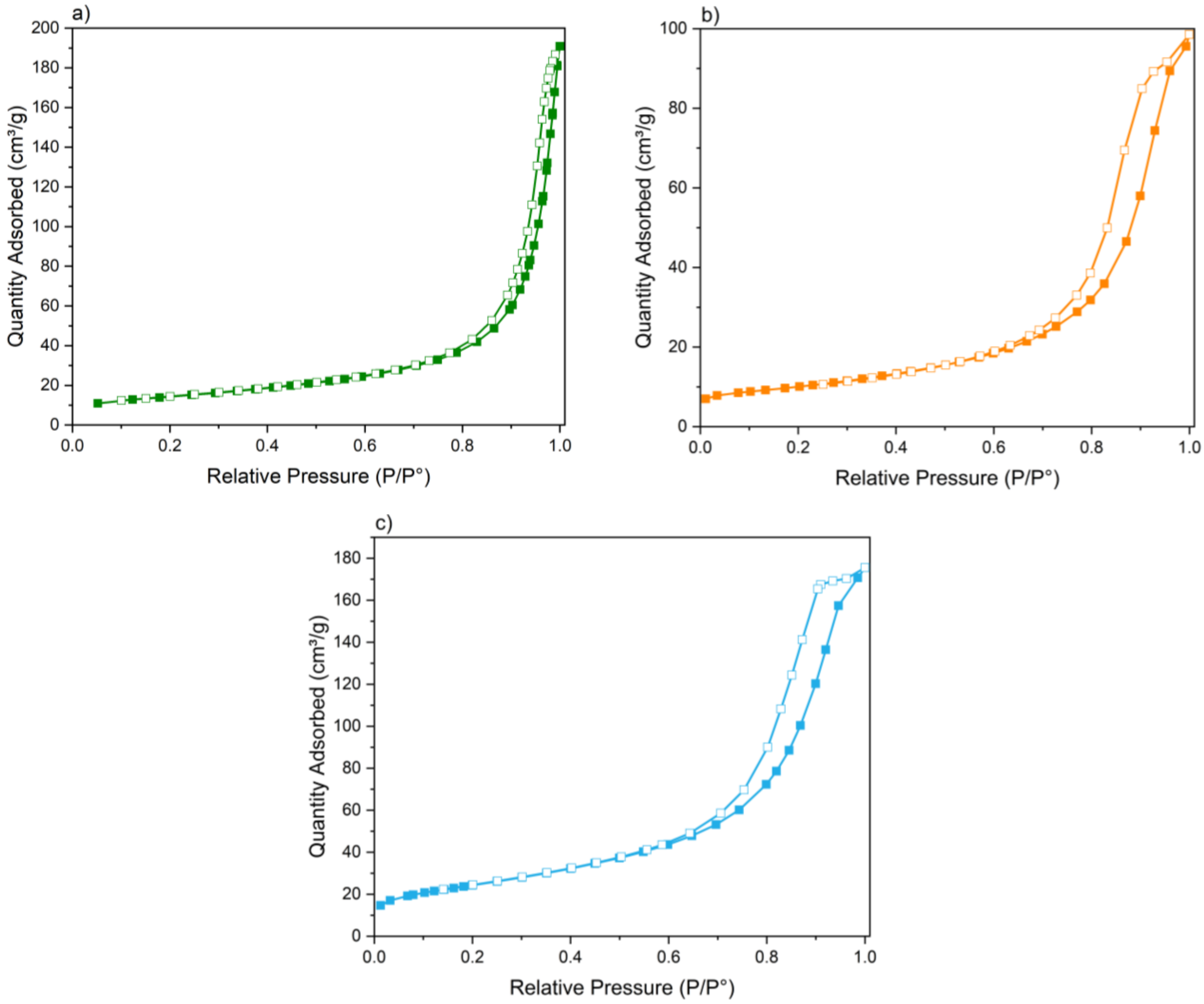


Figure S1. N_2 adsorption-desorption isotherms of the calcined (a) 1%$NaFe_3O_4$_WI, (b) 5%$NaFe_3O_4$_WI and (c) $NaFe_3O_4$_CP.

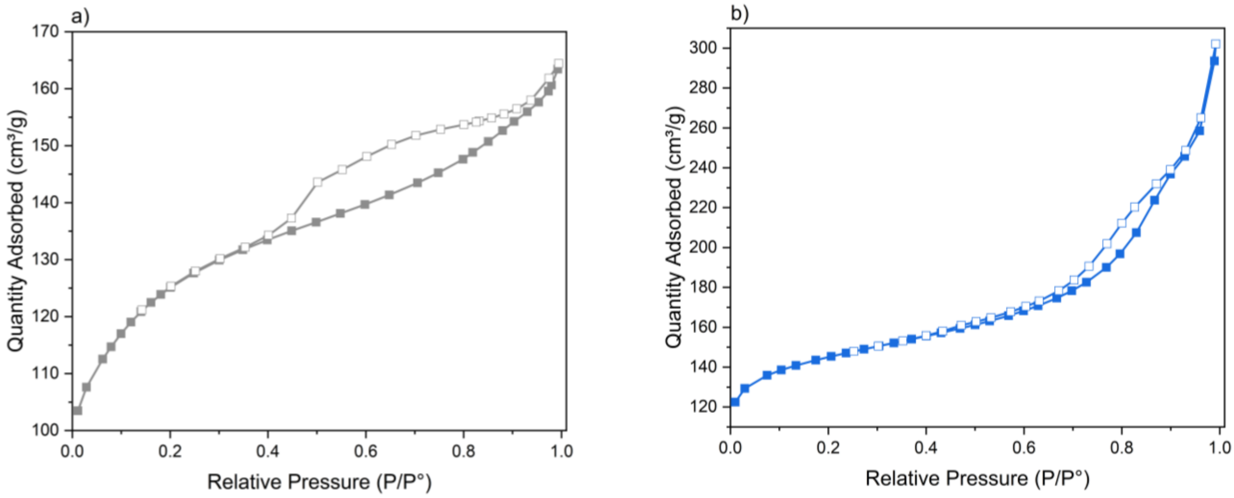


Figure S2. N_2 adsorption-desorption isotherms of the calcined (a) HZSM5 and (b) HZ.

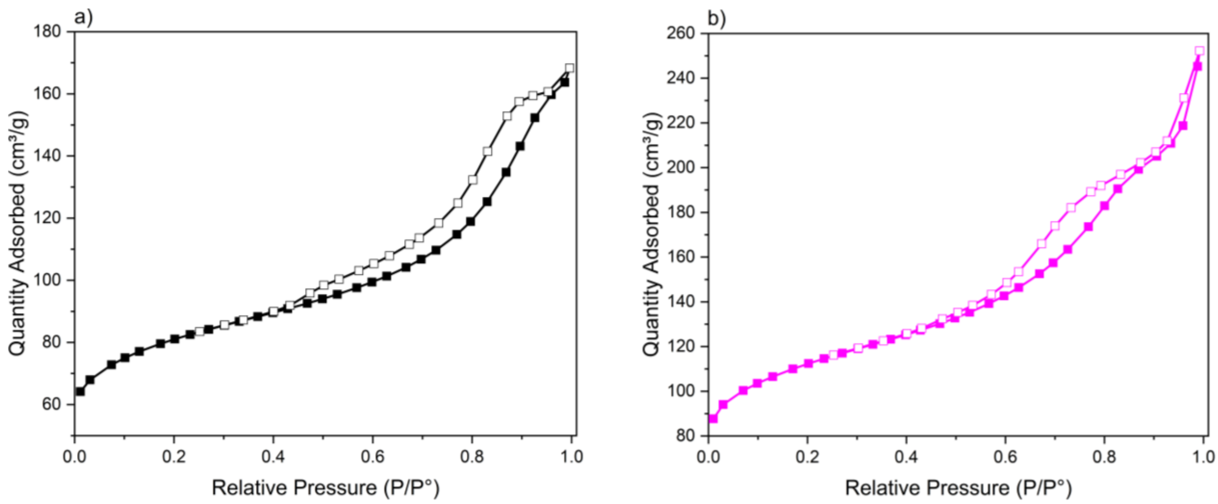


Figure S3. N_2 adsorption-desorption isotherms of the calcined (a) $NaFe_3O_4$_CP@HZSM5, (b) $NaFe_3O_4$_CP@HZ.

1.2 Crystallite size iron-oxide phases

Table S1: Crystalline size fresh iron phase calculated with Scherrer equation, based on the broadening of the most intense peak (311) at 2 Theta: 35.52 °

	Crystalline size *fresh* Fe_3O_4 *(nm)*	Crystalline size spent Fe_3O_4 *(nm)*
1%Na-Fe_3O_4_WI	17.8	31.6
5%Na-Fe_3O_4_WI	11.7	22.0
Na-Fe_3O_4 _CP	11.4	16.6

1.3 XRD in situ

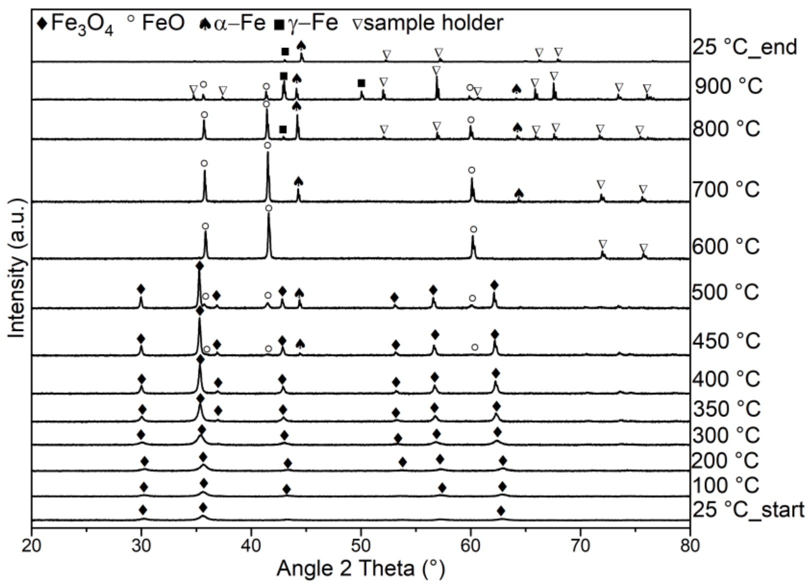
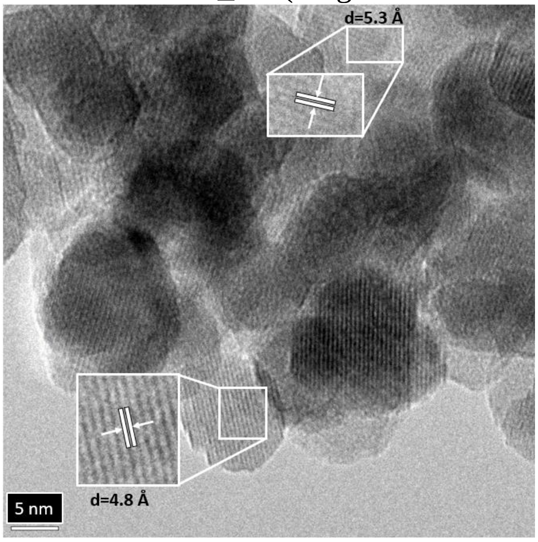


Figure S4. In situ XRD patterns of fresh $NaFe_3O_4$_CP catalytic powder under reducing atmosphere H_2/Ar from 25°C to 900°C.

1.4 HR-TEM measurements

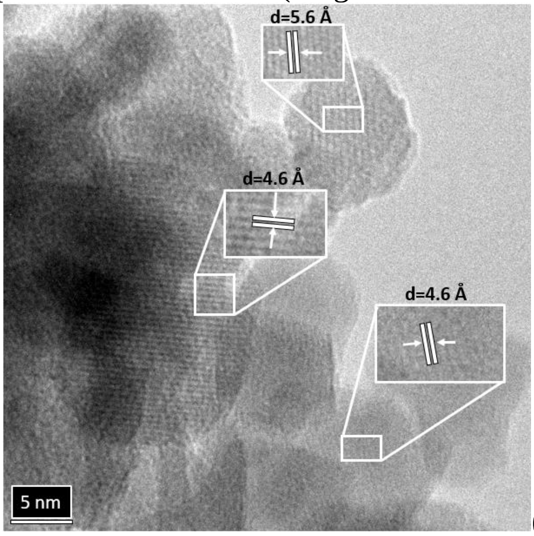
Fresh 1%$NaFe_3O_4$_WI (Magnification: 400 kX)



(a)

4.8 and 5.3 Å → [h k l] = 1:1:1 (Fe_3O_4)

Spent 1%$NaFe_3O_4$_WI (Magnification: 500 kX)

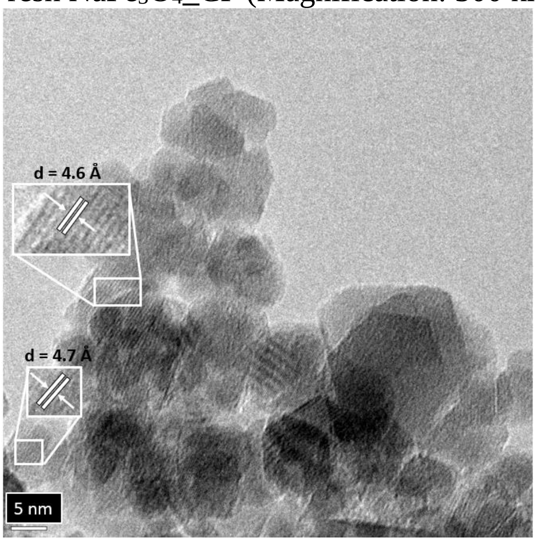


(b)

5.6 Å → [h k l] = 2:0:0 (Fe_2C_5)
4.6 Å → [h k l] = 1:1:1 (Fe_3O_4)

Figure S5. HR-TEM images of (a) fresh and (b) spent 1%$NaFe_3O_4$_WI.

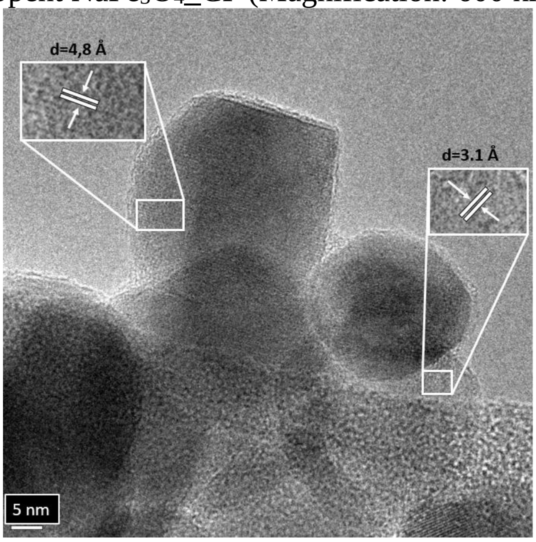
Fresh $NaFe_3O_4$_CP (Magnification: 300 kX)



(a)

4.6 and 4.7 Å → [h k l] = 1:1:1 (Fe_3O_4)

Spent $NaFe_3O_4$_CP (Magnification: 600 kX)



(b)

3.1 Å → [h k l] = 1:1:1 (Fe_2C_5)
4.8 Å → [h k l] = 1:1:1 di Fe_3O_4

Figure S6. HR-TEM images of (a) fresh and (b) spent $NaFe_3O_4$_CP.

Spent $NaFe_3O_4$_CP (Magnification: 150 kX)

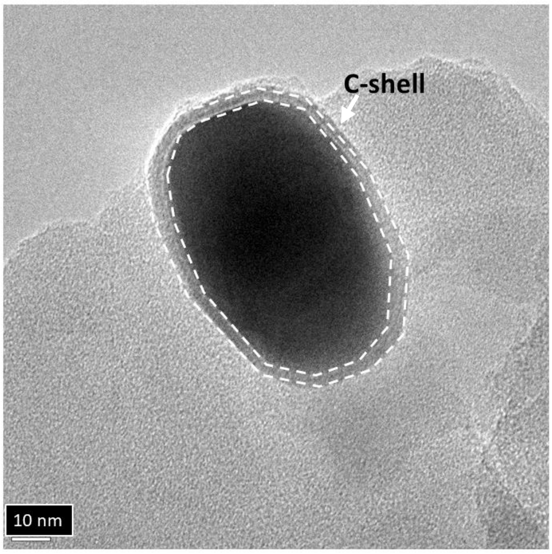


Figure S7. HR-TEM images of spent $NaFe_3O_4$_CP.

1.5 TEM and SEM measurements on the HZ sample

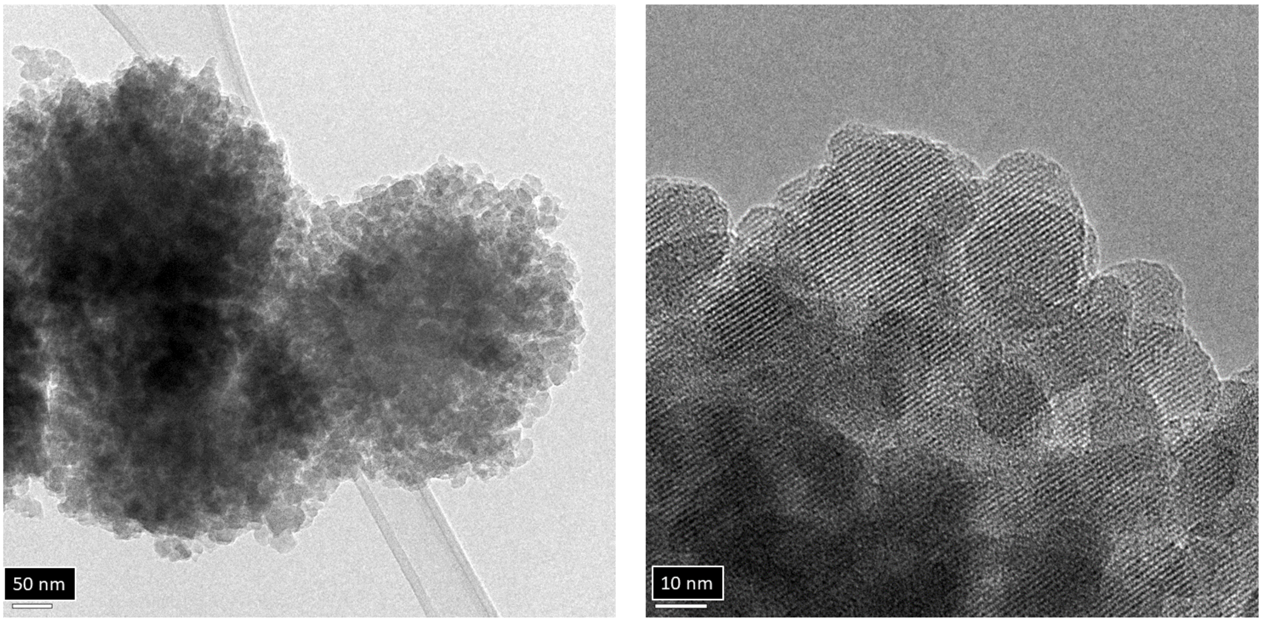


Figure S8. TEM images of the homemade HZ sample.

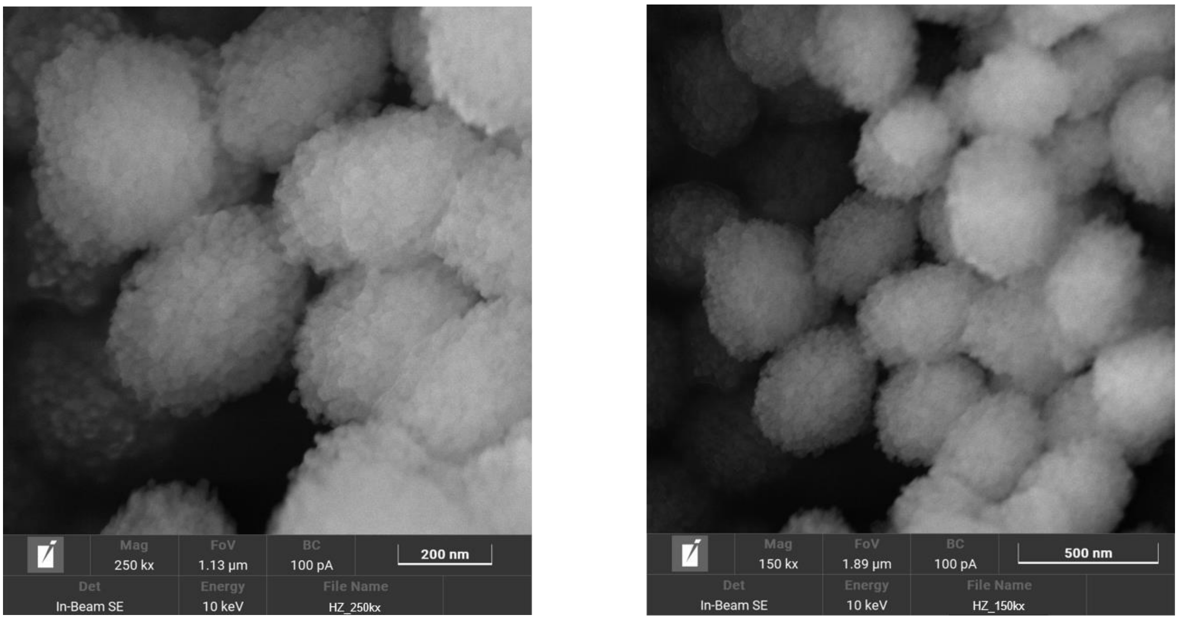


Figure S9. SEM images of the homemade HZ sample.

1.6 H_2-TPR measurements

Table S2. Quantitative analysis of the H_2-TPR measurements.

	T maximum (°C)	**H_2 uptake (mmol·g^{-1})**	**H_2 uptake/theoretical H_2 uptake (%)**
	438	1.5	8
1%NaFe$_3$O$_4$_WI	600	2.0	11
	788	13.9	80
	418	1.8	10
5%NaFe$_3$O$_4$_WI	618	7.4	41
	788	8.8	48
	362	1.6	9
NaFe$_3$O$_4$_CP	639	9.5	55
	788	6.2	36
	370	1.4	8
NaFe$_3$O$_4$_CP@HZSM5	617	9.2	53
	724	6.6	38
	453	1.5	9
NaFe$_3$O$_4$_CP@HZ	663	8.7	50
	809	7.1	41

1.7 NH_3-TPD measurements

Table S3. Quantitative analysis of the NH_3-TPD measurements.

	Weak acid sites	**Medium acid sites**	**Strong acid sites**	**Total acid sites**
	$\mu mol \cdot g^{-1}_{zeolite}$	**$\mu mol \cdot g^{-1}_{zeolite}$**	**$\mu mol \cdot g^{-1}_{zeolite}$**	**$\mu mol \cdot g^{-1}_{zeolite}$**
	(170-200°C)	**(~244°C)**	**(350-400°C)**	
HZSM-5	137.28	-	125.94	263.22
HZ	135.96	-	136.74	272.70
NaFe3O4_CP@HZSM5	77.81	190.86	-	268.66
NaFe3O4_CP@HZ	75.89	192.58	-	268.47

1.8 XPS measurements

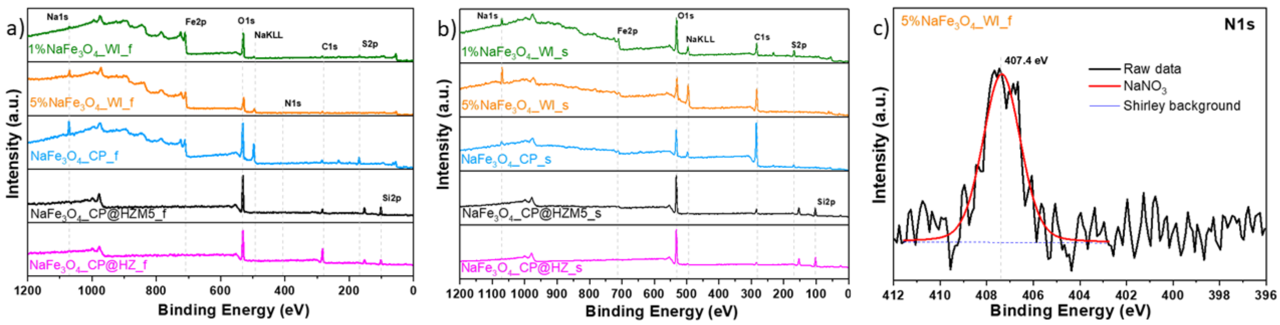
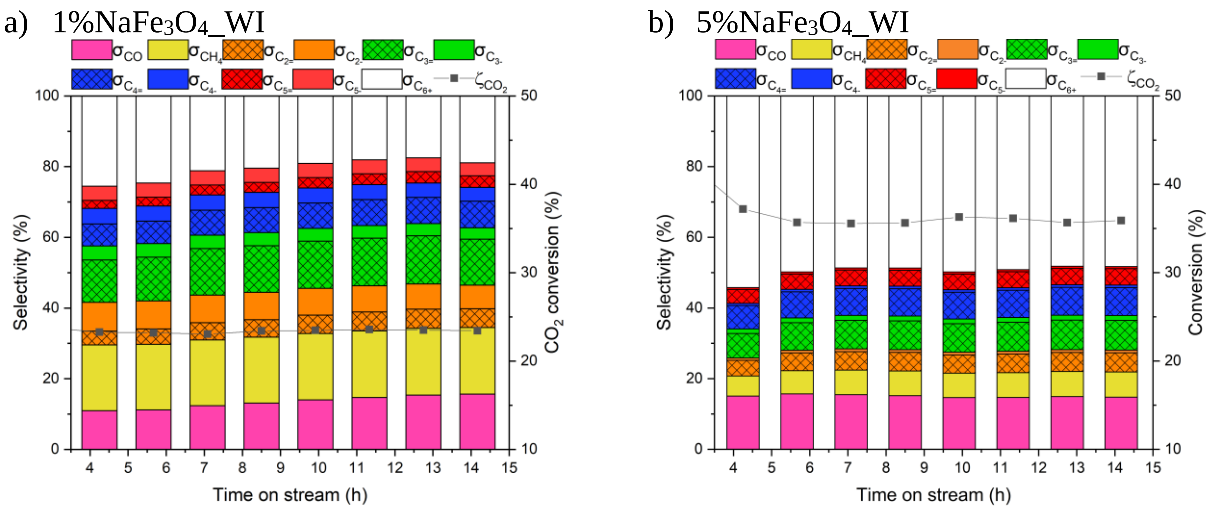


Figure S10. XPS spectra related to survey regions for fresh (a) and spent (b) samples. C) HR N1s region deconvoluted to show the chemical shift of N due to $NaNO_3$ bond in 5%$NaFe_3O_4$_WI_f sample.

1.9 TOS monitoring



c) NaFe3O4_CP

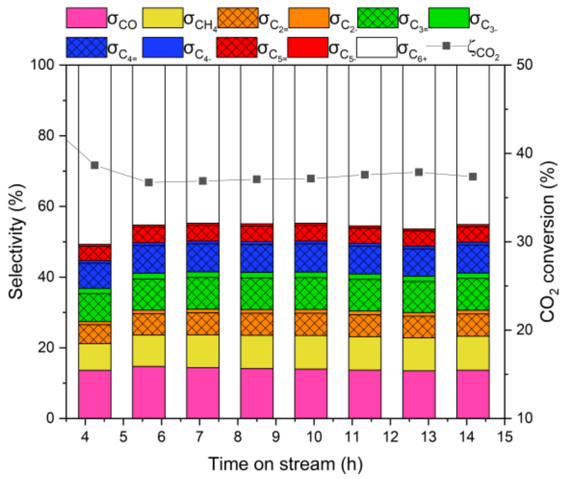


Figure S11. Time-on-stream (TOS) tests up to ≈ 14 hours, temperature: 330 °C, pressure: 2.3 MPa, and flow rate: 22 $NL \cdot g^{-1}_{Fe3O4} \cdot h^{-1}$ with an inlet $H_2/CO_2/N_2$ molar ratio equal to 15/5/3: a) 1%$NaFe_3O_4$_WI; b) 5%$NaFe_3O_4$_WI; c) $NaFe_3O_4$_CP.

Table S4. Results catalytic tests.

	CO_2 conv	**CO sel**	**CH_4 sel**	**C_2-$C_4^=$ sel**	**C_2-C_4^0 sel**	**C_{5+} sel**	**Ox sel**	**O/(O+P)[a]**
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
1%$NaFe_3O_4$_WI	22	13	19	25	16	25	2	62
5%$NaFe_3O_4$_WI	36	15	7	21	3	48	7	88
$NaFe_3O_4$_CP	38	14	9	23	3	42	8	87
$NaFe_3O_4$_CP+HZSM5	35	19	8	5	12	53	2	28
$NaFe_3O_4$_CP+HZ	40	12	8	3	12	64	1	18
$NaFe_3O_4$_CP@HZSM5	22	12	24	7	33	25	0	18
$NaFe_3O_4$_CP@HZ	25	18	19	10	25	27	0	29

[a] Olefin share calculated for the fraction C_2-C_4.

1.10 Results Ox compounds derived from TOC analysis

Table S5. Results derived from TOC and HPLC.

	TOC $mg_C \cdot L^{-1}$	**HPLC[a] $mg_C \cdot L^{-1}$**
1%$NaFe_3O_4$_WI	7133	896
5%$NaFe_3O_4$_WI	30335	6662
$NaFe_3O_4$_CP	5960	338
$NaFe_3O_4$_CP+HZSM5	9015	2565
$NaFe_3O_4$_CP+HZ	4854	2151
$NaFe_3O_4$_CP@HZSM5	1581	863
$NaFe_3O_4$_CP@HZ	998	249

[a]$mg \cdot L^{-1}$ of acetone resulting from reactor and lines cleaning.

1.11 Chromatograms of the oil injected in the GC-MS

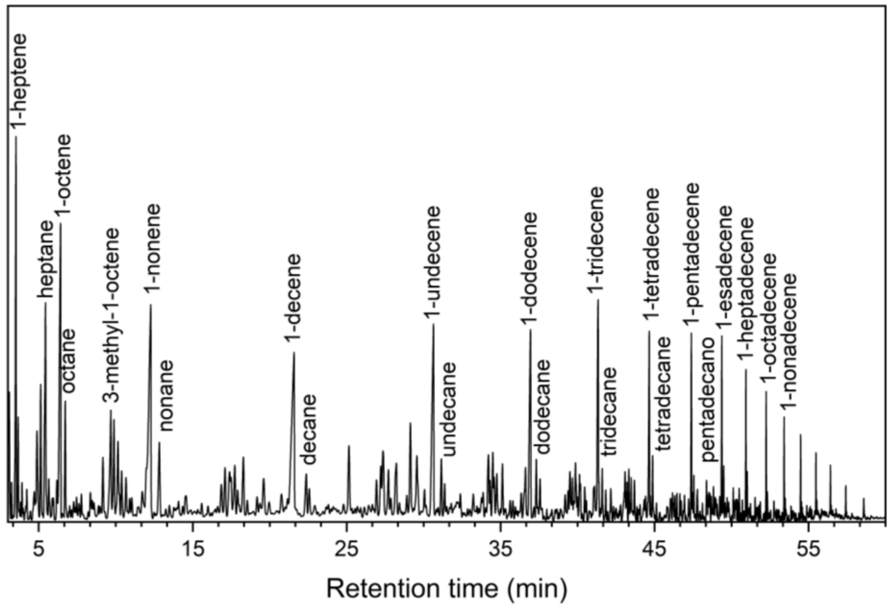


Figure S12. $NaFe_3O_4$ _CP.

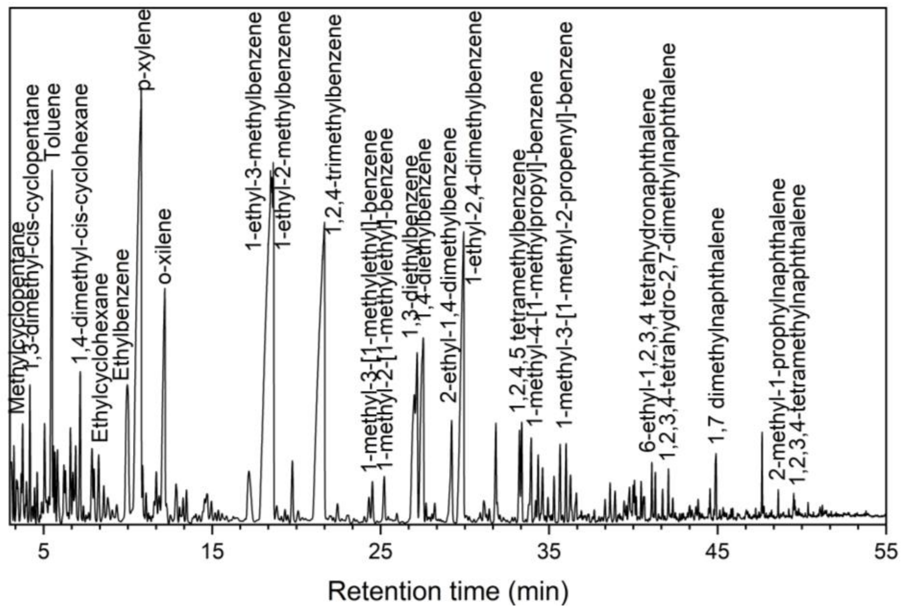


Figure S13. $NaFe_3O_4$ _CP+HZSM-5.

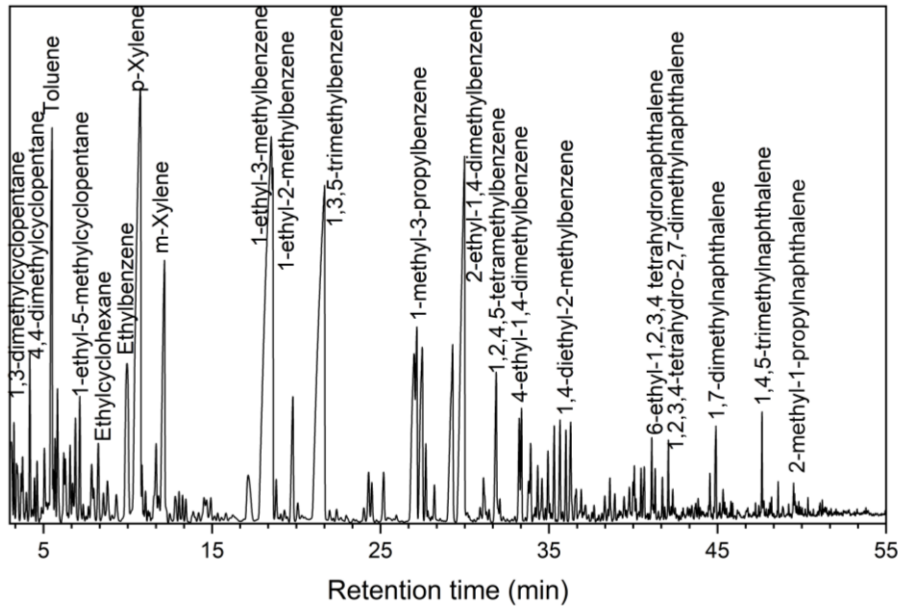


Figure S14. $NaFe_3O_4$ _CP+HZ.