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Original

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

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1.1 N_2 physisorption measurements

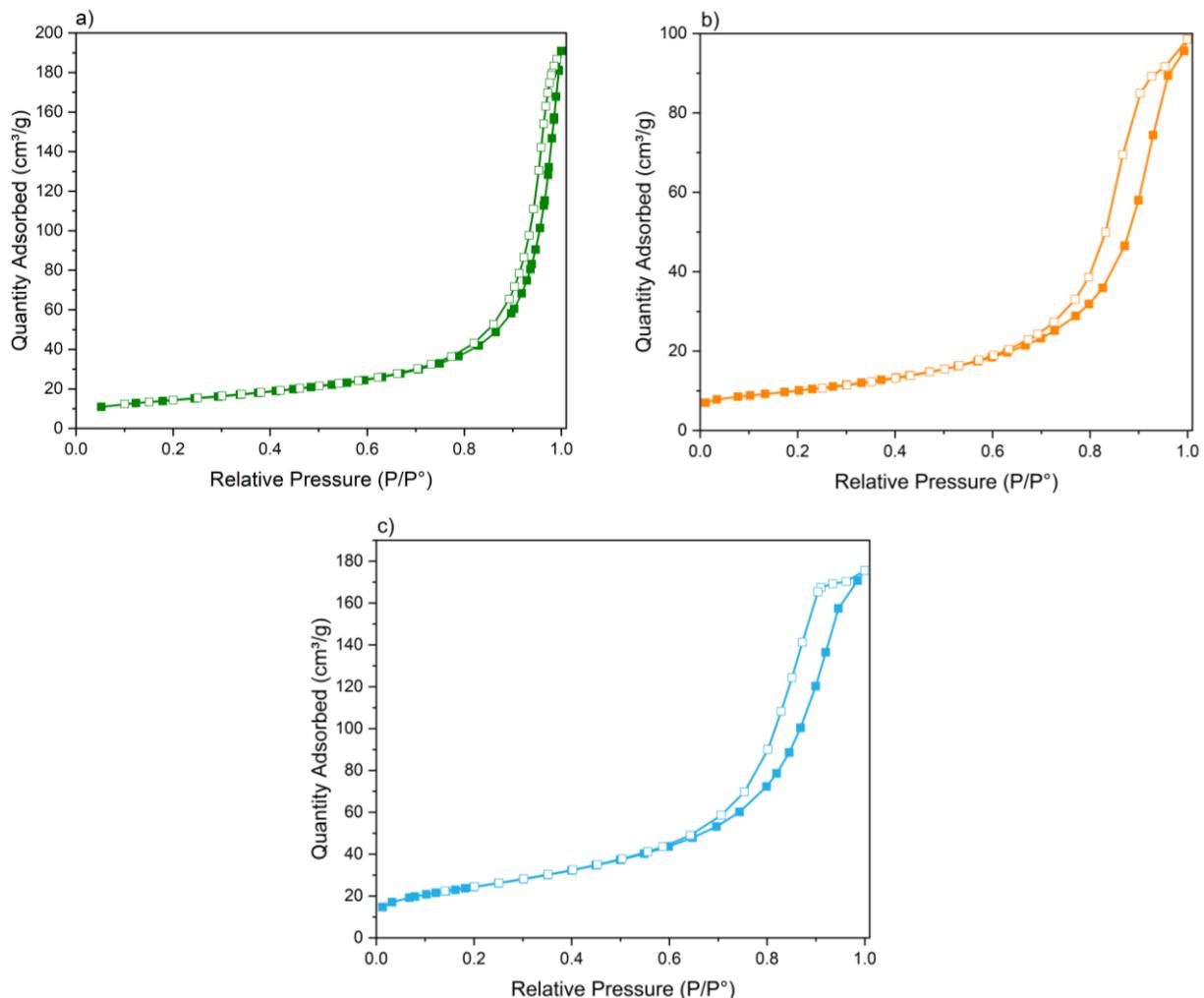


Figure S1. N_2 adsorption-desorption isotherms of the calcined (a) 1%NaFe₃O₄-WI, (b) 5%NaFe₃O₄-WI and (c) NaFe₃O₄-CP.

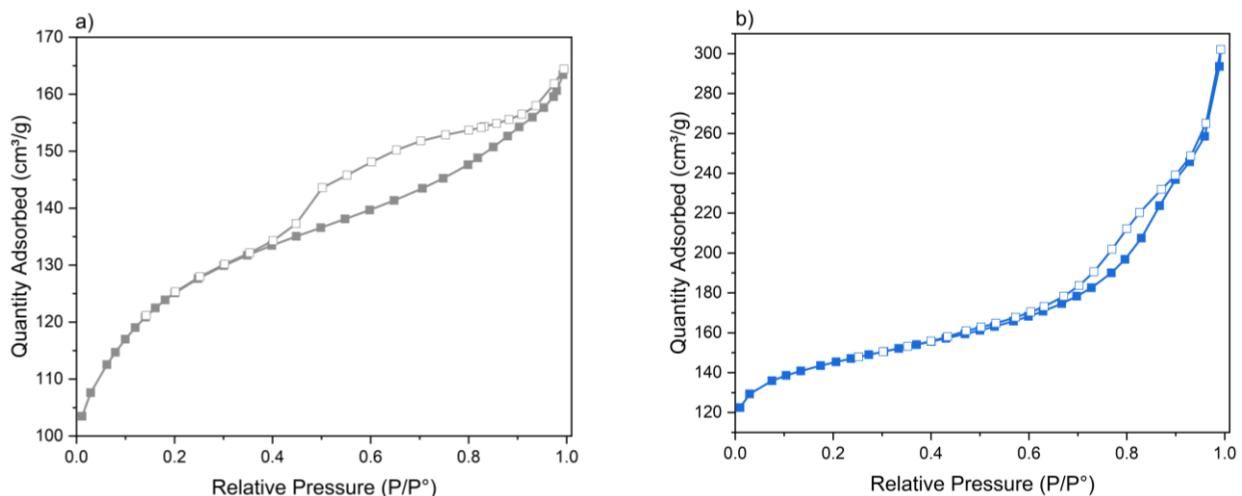


Figure S2. N_2 adsorption-desorption isotherms of the calcined (a) HZSM5 and (b) HZ.

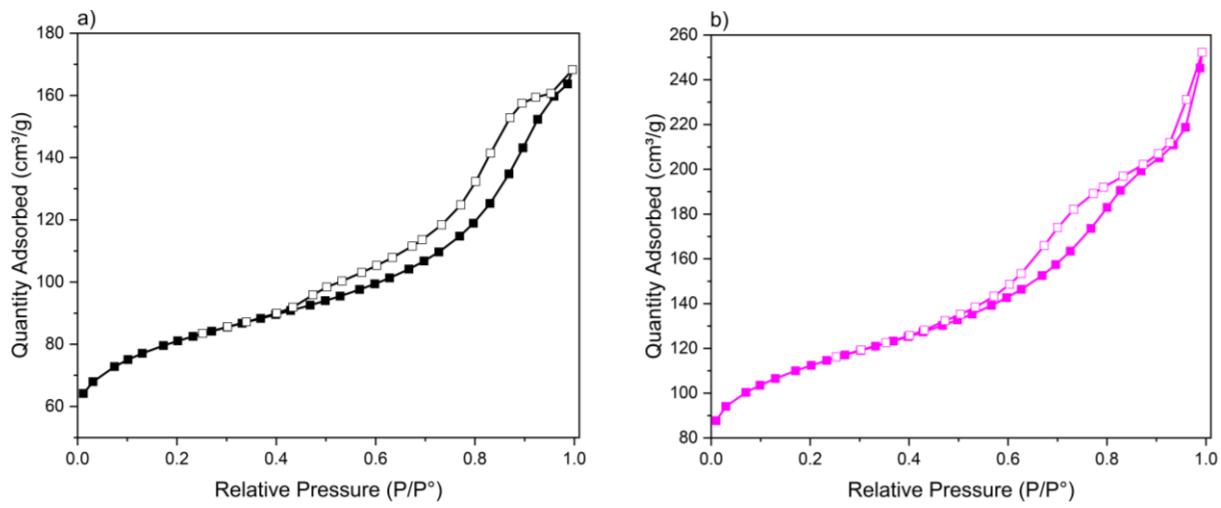


Figure S3. N_2 adsorption-desorption isotherms of the calcined (a) $\text{NaFe}_3\text{O}_4\text{-CP}@\text{HZSM}5$, (b) $\text{NaFe}_3\text{O}_4\text{-CP}@\text{HZ}$.

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*

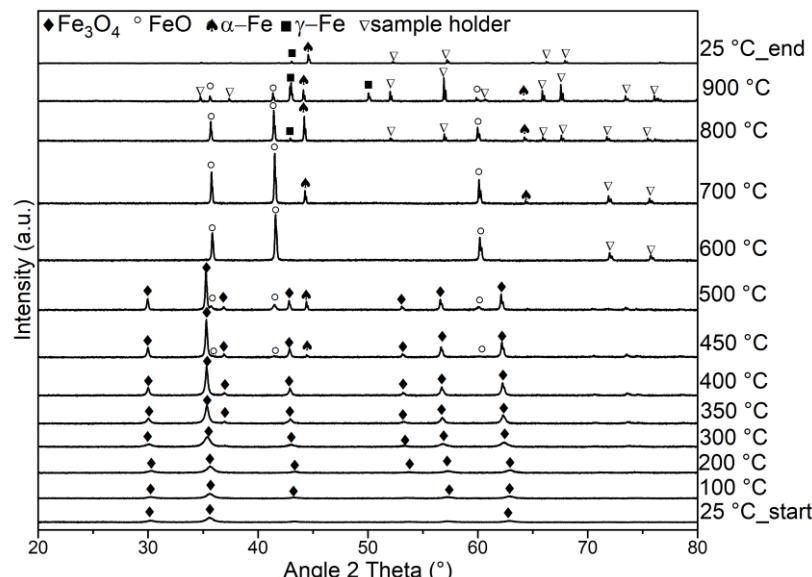
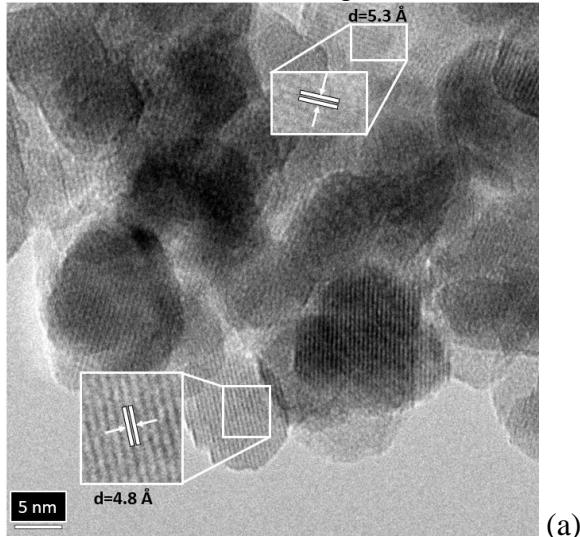


Figure S4. In situ XRD patterns of fresh $\text{NaFe}_3\text{O}_4\text{-CP}$ catalytic powder under reducing atmosphere H_2/Ar from 25°C to 900°C.

1.4 HR-TEM measurements

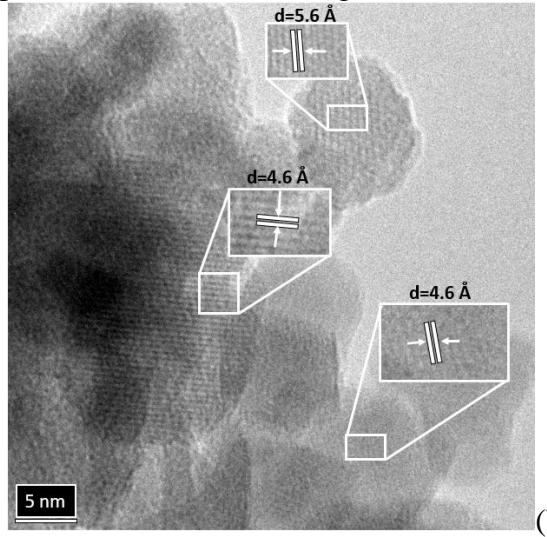
Fresh 1%NaFe₃O₄_WI (Magnification: 400 kX)



$4.8 \text{ and } 5.3 \text{ \AA} \rightarrow [h \text{ } k \text{ } l] = 1:1:1 \text{ (Fe}_3\text{O}_4)$

(a)

Spent 1%NaFe₃O₄_WI (Magnification: 500 kX)

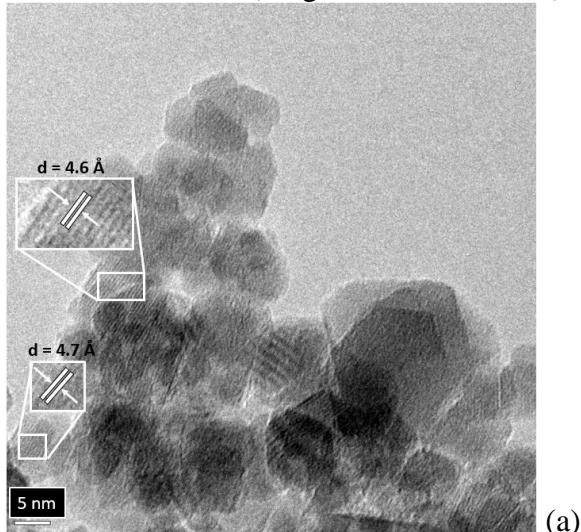


$5.6 \text{ \AA} \rightarrow [h \text{ } k \text{ } l] = 2:0:0 \text{ (Fe}_2\text{C}_5)$
 $4.6 \text{ \AA} \rightarrow [h \text{ } k \text{ } l] = 1:1:1 \text{ (Fe}_3\text{O}_4)$

(b)

Figure S5. HR-TEM images of (a) fresh and (b) spent 1%NaFe₃O₄_WI.

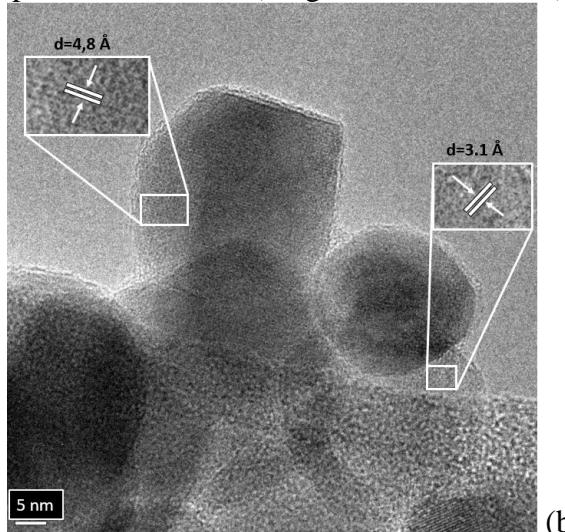
Fresh NaFe₃O₄_CP (Magnification: 300 kX)



$4.6 \text{ and } 4.7 \text{ \AA} \rightarrow [h \text{ } k \text{ } l] = 1:1:1 \text{ (Fe}_3\text{O}_4)$

(a)

Spent NaFe₃O₄_CP (Magnification: 600 kX)



$3.1 \text{ \AA} \rightarrow [h \text{ } k \text{ } l] = 1:1:1 \text{ (Fe}_2\text{C}_5)$
 $4.8 \text{ \AA} \rightarrow [h \text{ } k \text{ } l] = 1:1:1 \text{ di Fe}_3\text{O}_4$

(b)

Figure S6. HR-TEM images of (a) fresh and (b) spent NaFe₃O₄_CP.

Spent NaFe₃O₄_CP (Magnification: 150 kX)

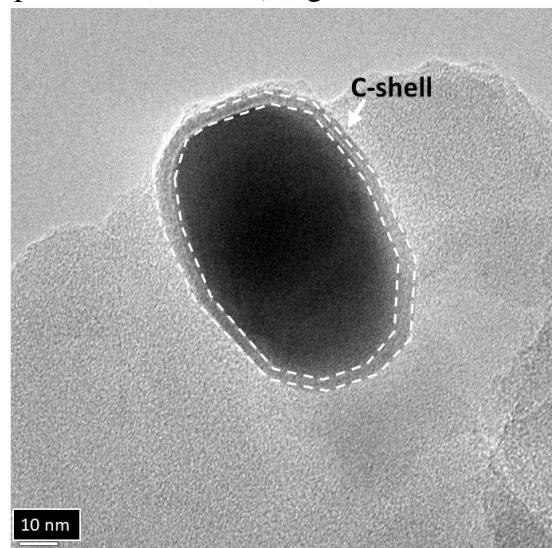


Figure S7. HR-TEM images of spent NaFe₃O₄_CP.

1.5 TEM and SEM measurements on the HZ sample

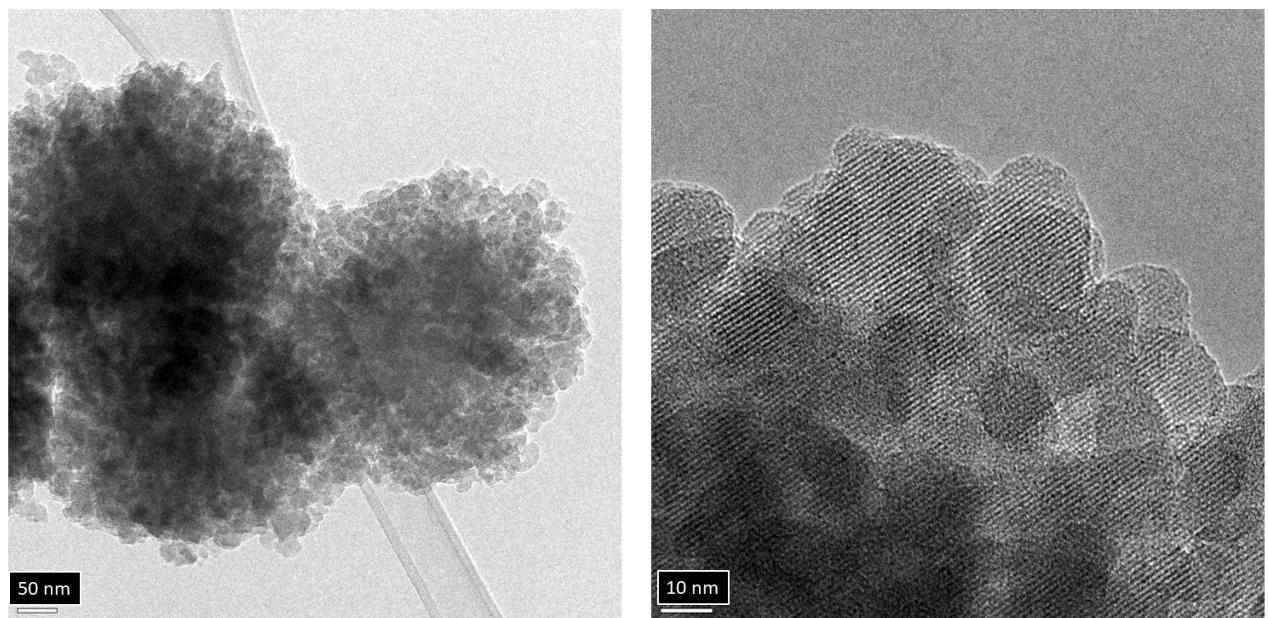


Figure S8. TEM images of the homemade HZ sample.

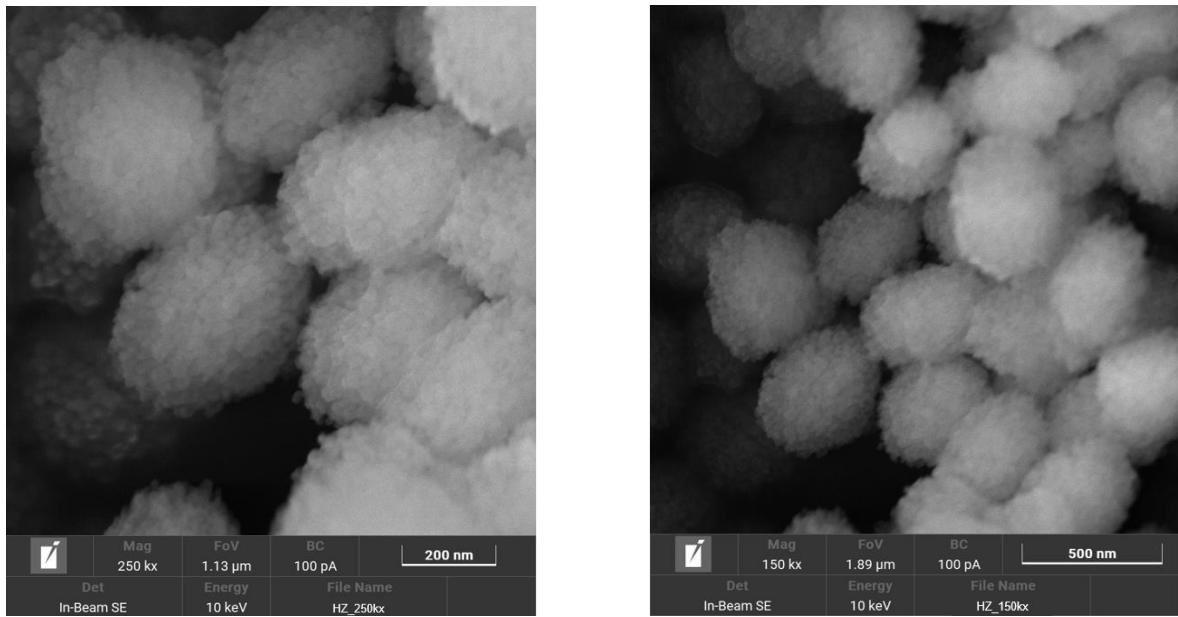


Figure S9. SEM images of the homemade HZ sample.

1.6 H_2 -TPR measurements

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

	T maximum (°C)	H_2 uptake ($\text{mmol}\cdot\text{g}^{-1}$)	H_2 uptake/theoretical H_2 uptake (%)
1%NaFe₃O₄_WI	438	1.5	8
	600	2.0	11
	788	13.9	80
5%NaFe₃O₄_WI	418	1.8	10
	618	7.4	41
	788	8.8	48
NaFe₃O₄_CP	362	1.6	9
	639	9.5	55
	788	6.2	36
NaFe₃O₄_CP@H_{ZS} M5	370	1.4	8
	617	9.2	53
	724	6.6	38
NaFe₃O₄_CP@HZ	453	1.5	9
	663	8.7	50
	809	7.1	41

1.7 NH₃-TPD measurements

Table S3. Quantitative analysis of the NH₃-TPD measurements.

	Weak acid sites μmol·g ⁻¹ zeolite (170–200°C)	Medium acid sites μmol·g ⁻¹ zeolite (~244°C)	Strong acid sites μmol·g ⁻¹ zeolite (350–400°C)	Total acid sites μmol·g ⁻¹ zeolite
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

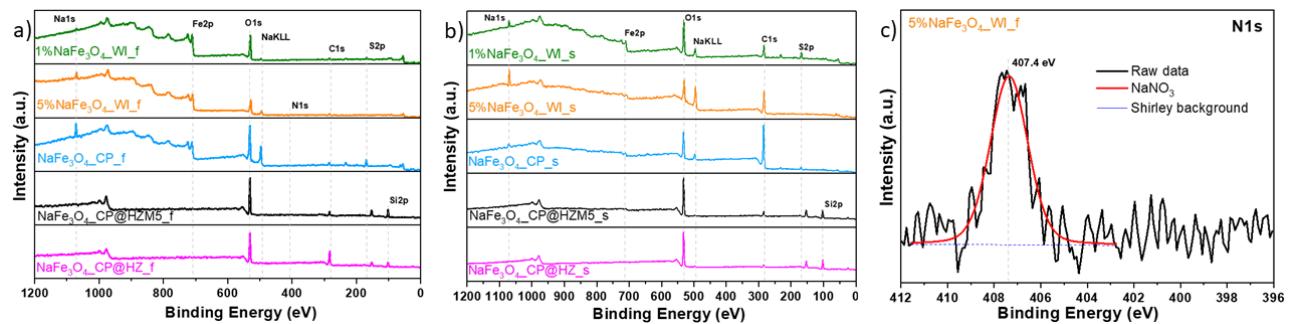
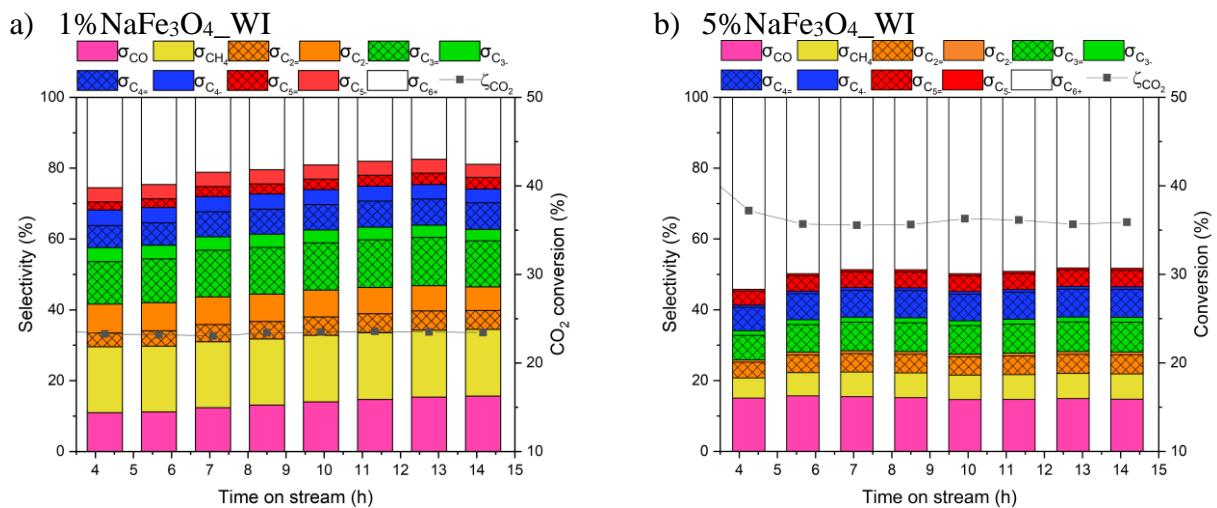


Figure S10. XPS spectra related to survey regions for fresh (a) and spent (b) samples. C) HR N1s region deconvoluted to show the chemical shift of N due to NaNO₃ bond in 5% NaFe₃O₄_WI_f sample.

1.9 TOS monitoring



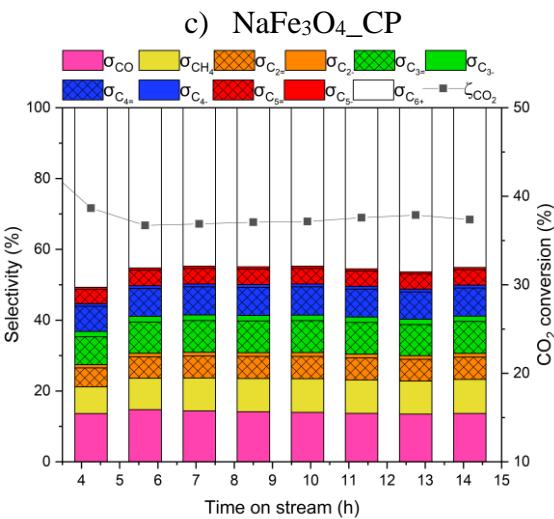


Figure S11. Time-on-stream (TOS) tests up to \approx 14 hours, temperature: 330 °C, pressure: 2.3 MPa, and flow rate: 22 NL·g⁻¹_{Fe3O4}·h⁻¹ with an inlet H₂/CO₂/N₂ molar ratio equal to 15/5/3: a) 1%NaFe₃O₄_WI; b) 5%NaFe₃O₄_WI; c) NaFe₃O₄_CP.

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 ₃ O ₄ _WI	22	13	19	25	16	25	2	62
5%NaFe ₃ O ₄ _WI	36	15	7	21	3	48	7	88
NaFe ₃ O ₄ _CP	38	14	9	23	3	42	8	87
NaFe ₃ O ₄ _CP+HZSM5	35	19	8	5	12	53	2	28
NaFe ₃ O ₄ _CP+HZ	40	12	8	3	12	64	1	18
NaFe ₃ O ₄ _CP@HZSM5	22	12	24	7	33	25	0	18
NaFe ₃ O ₄ _CP@HZ	25	18	19	10	25	27	0	29

^a Olefin share calculated for the fraction C₂-C₄.

1.10 Results Ox compounds derived from TOC analysis

Table S5. Results derived from TOC and HPLC.

	TOC mgc·L ⁻¹	HPLC ^a mgc·L ⁻¹
1%NaFe ₃ O ₄ _WI	7133	896
5%NaFe ₃ O ₄ _WI	30335	6662
NaFe ₃ O ₄ _CP	5960	338
NaFe ₃ O ₄ _CP+HZSM5	9015	2565
NaFe ₃ O ₄ _CP+HZ	4854	2151
NaFe ₃ O ₄ _CP@HZSM5	1581	863
NaFe ₃ O ₄ _CP@HZ	998	249

^amg·L⁻¹ of acetone resulting from reactor and lines cleaning.

1.11 Chromatograms of the oil injected in the GC-MS

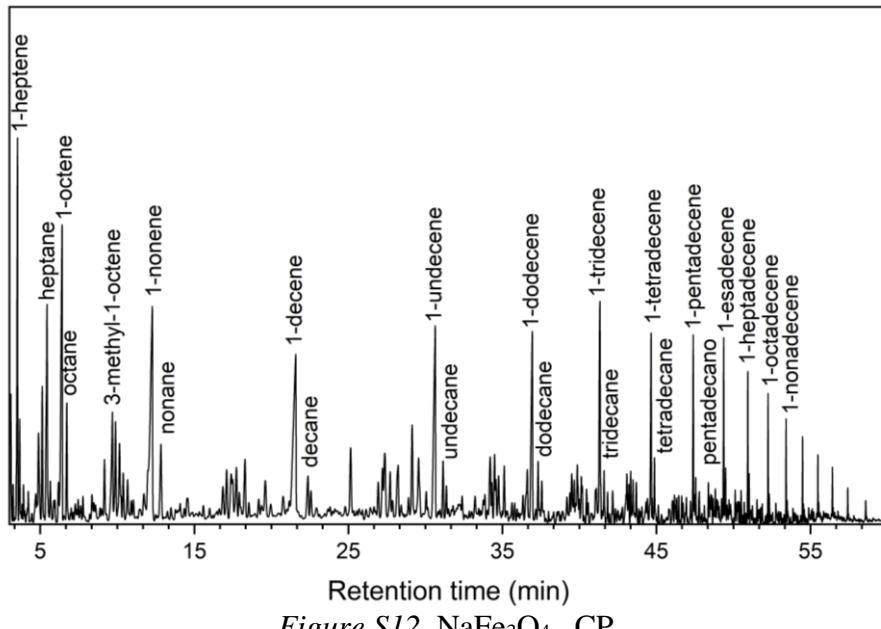


Figure S12. NaFe₃O₄ _CP.

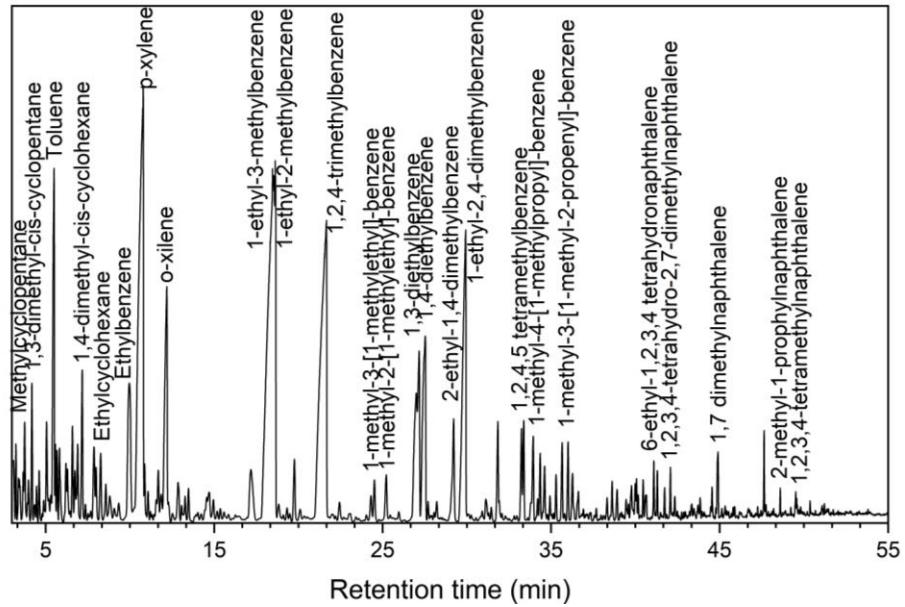


Figure S13. NaFe₃O₄ _CP+HZSM-5.

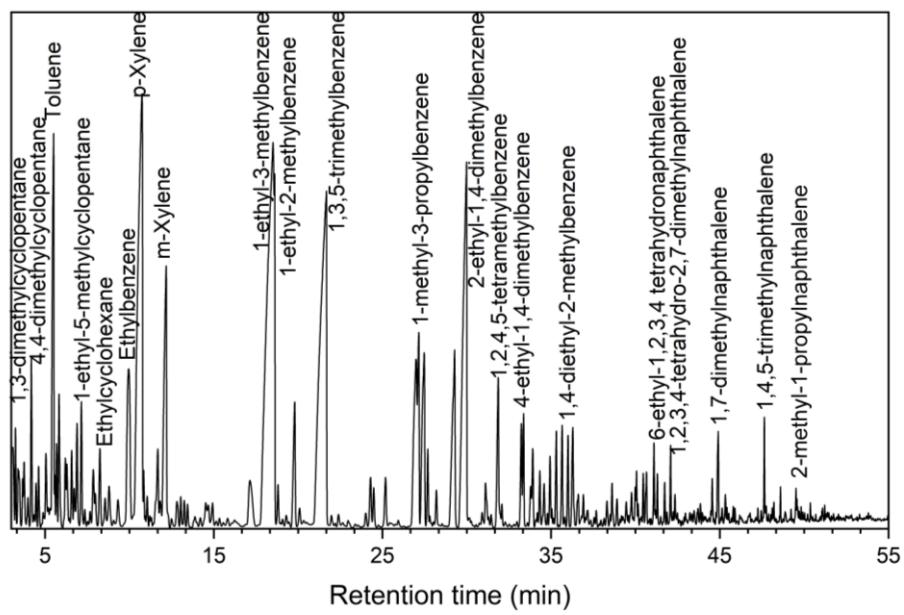


Figure S14. NaFe_3O_4 _CP+HZ.