CO₂ conversion into hydrocarbons via modified Fischer-Tropsch

synthesis by using bulk iron catalysts combined with zeolites.

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Figure S2. N₂ adsorption-desorption isotherms of the calcined (a) HZSM5 and (b) 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 <i>fresh</i> Fe ₃ O ₄ (<i>nm</i>)	Crystalline size spent Fe ₃ O ₄ (<i>nm</i>)
1%Na-Fe3O4_WI	17.8	31.6
5%Na-Fe3O4_WI	11.7	22.0
Na-Fe ₃ O ₄ _CP	11.4	16.6

1.3 XRD in situ



Figure S4. In situ XRD patterns of fresh NaFe₃O₄_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)

Spent 1%NaFe₃O₄_WI (Magnification: 500 kX)



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

Fresh NaFe₃O₄_CP (Magnification: 300 kX)



4.6 and 4.7 Å \rightarrow [h k l] = 1:1:1 (Fe₃O₄)







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 H₂-TPR measurements

	T maximum (°C)	H2 uptake (mmol·g ⁻¹)	H2 uptake/theoretical H2 uptake (%)
	438	1.5	8
1%NaFe3O4_WI	600	2.0	11
	788	13.9	80
	418	1.8	10
5%NaFe3O4_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
NaresU4_CP@HZ5	617	9.2	53
1115	724	6.6	38
	453	1.5	9
NaFe ₃ O ₄ _CP@HZ	663	8.7	50
	809	7.1	41

Table S2. Quantitative analysis of the H2-TPR measurements.

1.7 NH₃-TPD measurements

	Weak acid sites µmol·g ⁻¹ zeolite	Medium acid sites μmol·g ⁻¹ zeolite	Strong acid sites µmol·g ⁻¹ zeolite	Total acid sites μmol·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

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

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.

	CO ₂ conv	CO sel	CH4 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 C_2 - C_4 .

1.10 Results Ox compounds derived from TOC analysis

Table S5. Results derived from TOC and HPLC.

	TOC mg _C ·L· ¹	HPLC ^a mg _C ·L ⁻¹
1%NaFe3O4_WI	7133	896
5%NaFe3O4_WI	30335	6662
NaFe ₃ O ₄ _CP	5960	338
NaFe ₃ O ₄ _CP+HZSM5	9015	2565
NaFe3O4_CP+HZ	4854	2151
NaFe3O4_CP@HZSM5	1581	863
NaFe3O4_CP@HZ	998	249

 a mg·L⁻¹ of acetone resulting from reactor and lines cleaning.

Figure S13. NaFe₃O₄ _CP+HZSM-5.

Figure S14. NaFe₃O₄ _CP+HZ.