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22 October 2026

Tuning e-fuel product distribution by combining a Na-promoted Fe-based catalyst with BETA zeolites in CO_2-modified Fischer-Tropsch synthesis

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Supplementary Materials

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1. Experimental test bench

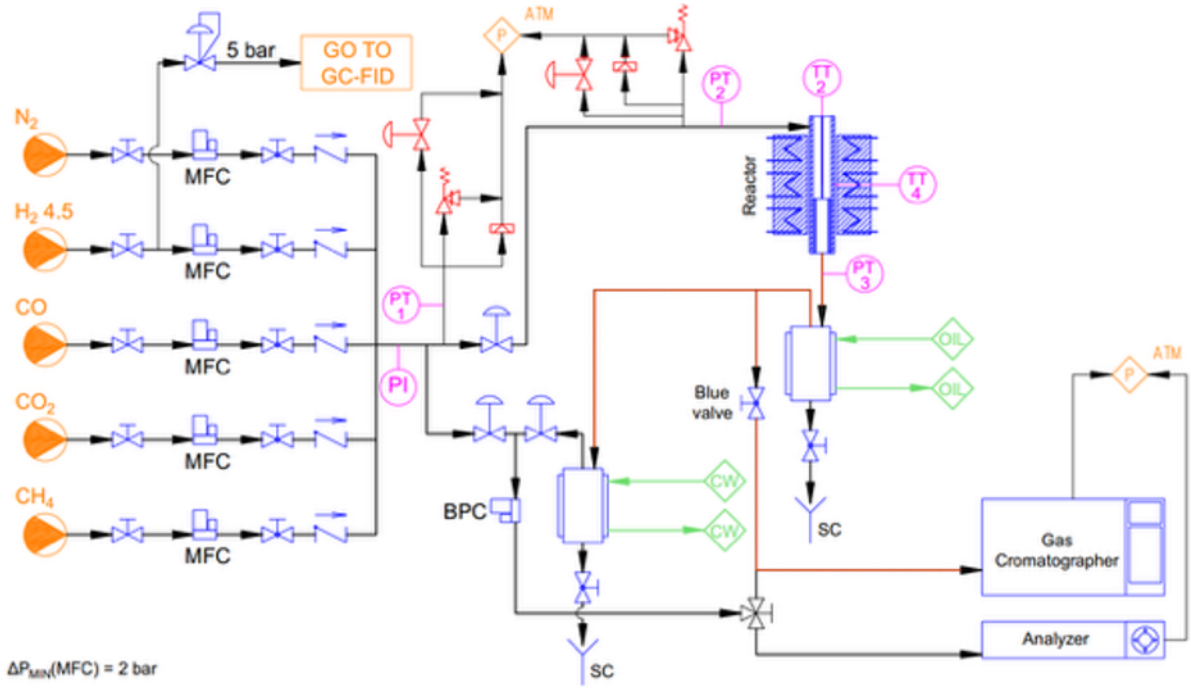

Figure S1. Scheme of the experimental test bench used for the catalytic tests.

2. Characterization of the fresh catalyst

2.1. N_2 physisorption analyses

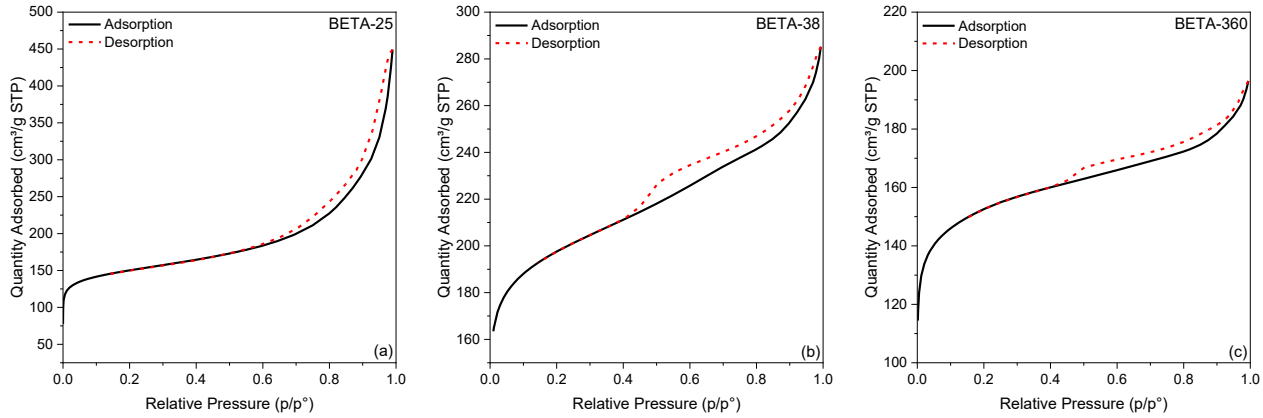

Figure S2. Adsorption and desorption curves after N_2 physisorption of the following samples: (a) BETA-25 fresh, (b) BETA-38 fresh, (c) BETA-360 fresh.

Table S1. Surface area, pore volume and average pore diameter of the fresh zeolites after N_2 physisorption

Sample	BET surface area	BJH pore volume	BJH desorption average pore diameter
	$m^2 \cdot g^{-1}$	$cm^3 \cdot g^{-1}$	Å
BETA-25	481	0.6	110
BETA-38	624	0.2	49
BETA-360	478	0.1	46

2.2. FE-SEM analyses

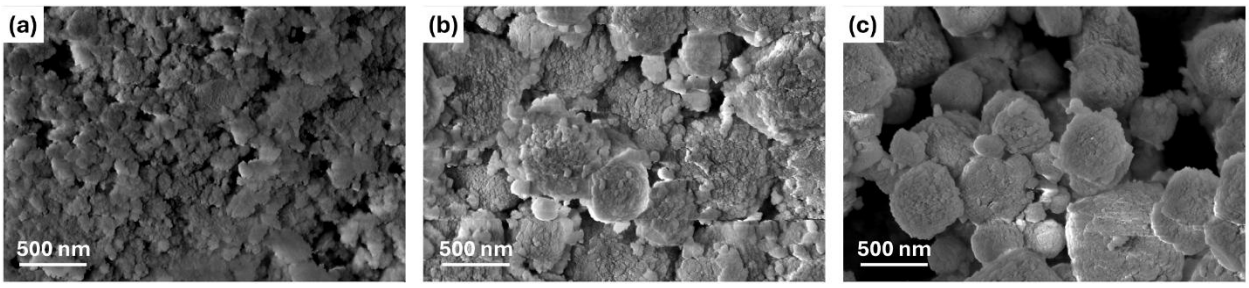

Figure S3. High-Resolution SEM images of fresh zeolites: (a) BETA-25, (b) BETA-38, (c) BETA-360 (magnification: 100 kX).

Table S2. SEM-EDS atomic percentage of the elements in the three fresh zeolites: BETA-25, BETA-38 and BETA-360.

Samples	Si (at. %)	Al (at. %)	O (at. %)	Si/Al	Nominal Si/Al
BETA-25	28.6	2.3	69.2	12.4	12.5
BETA-38	25.1	1.4	73.6	17.9	19
BETA-360	36.9	0.2	62.9	184.5	180

2.3. XRD measurements

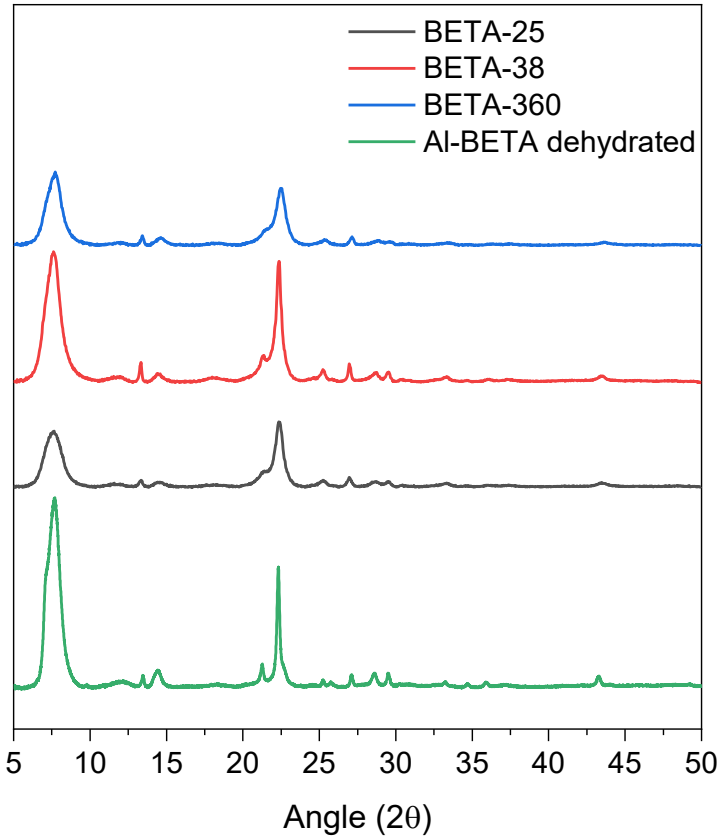

Figure S4. XRD patterns of the three fresh zeolites: BETA-25, BETA-38, BETA-360 collected over the 2θ range of 5°-50° by comparing it with reference pattern.

2.4. NH_3-TPD measurements and FTIR spectroscopy using CD_3CN

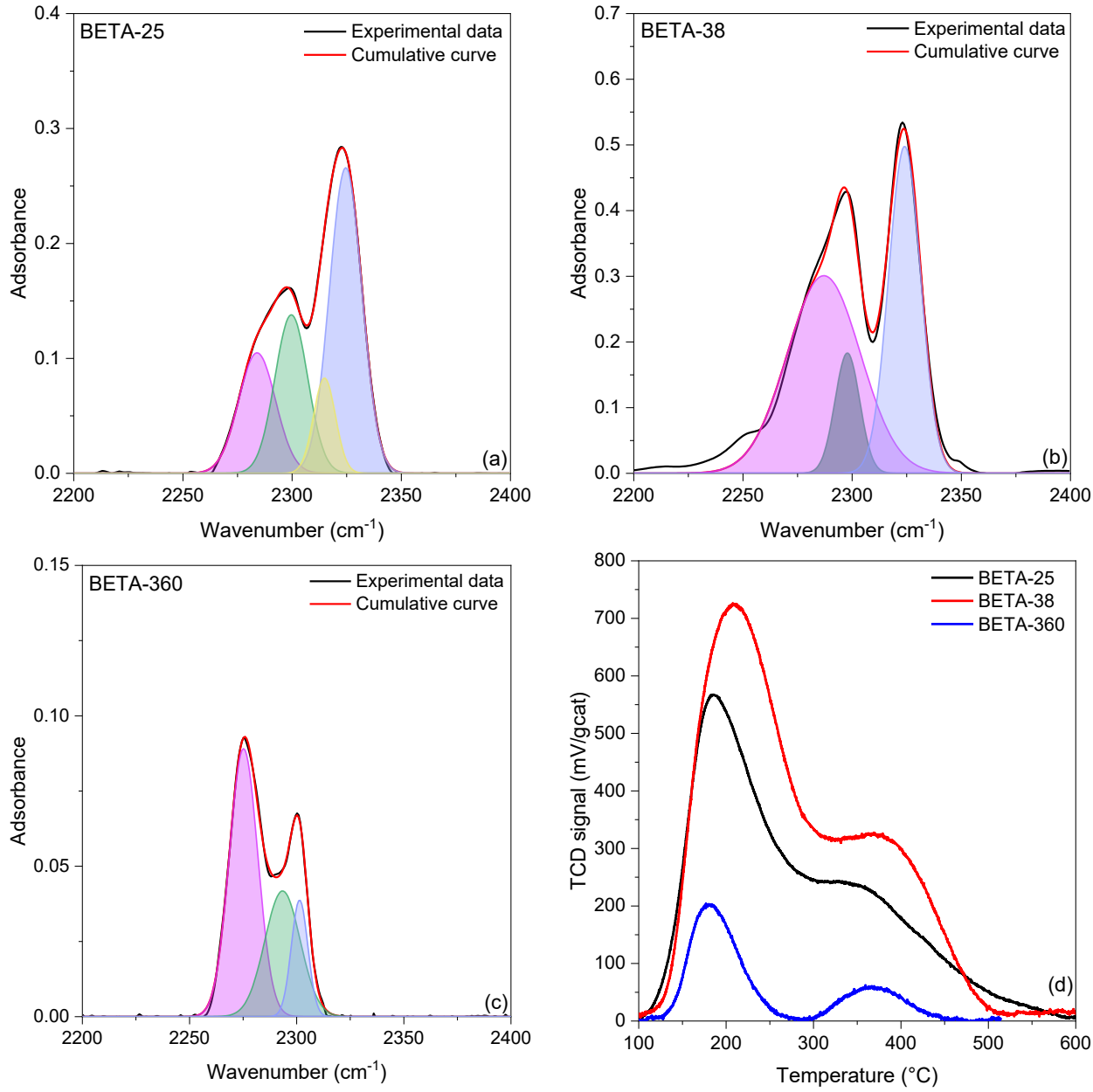

Figure S5. Absorbance profiles via FTIR spectroscopy using CD_3CN as a probe molecule for fresh zeolites: (a) BETA-25, (b) BETA-38, (c) BETA-360; (d) NH_3-TPD profiles of the three fresh zeolites: BETA-25, BETA-38, BETA-360.

3. Catalytic test results

3.1. HC selectivity

Table S3. Values of CO_2 conversion, CO selectivity and HCs selectivity of the tests with the addition of BETA zeolite compared to the test using only iron oxide. Reaction conditions: 7 $NL \cdot gFe_3O_4^{-1} \cdot h^{-1}$ ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe_3O_4, 2 g zeolite

Sample	ACB-25	ACB-38	ACB-360	ACB-38_DB	AC
ζ_{CO_2} (%)	38.3	42.4	43.0	44.2	36.9
σ_{CO} (%)	11.0	9.3	10.5	10.4	10.6
σ_{CH_4} (%) [(a)]	19.8	26.4	25.7	14.8	13.9
$\sigma_{C_{2=}}$ (%) [(a)]	7.7	8.3	8.5	8.3	7.8
$\sigma_{C_{2-}}$ (%) [(a)]	4.4	3.5	2.9	3.9	1.6
$\sigma_{C_{3=}}$ (%) [(a)]	13.0	12.2	12.5	13.9	11.7
$\sigma_{C_{3-}}$ (%) [(a)]	1.8	1.7	1.4	2.2	1.1
$\sigma_{C_{4=}}$ (%) [(a)]	5.2	4.1	4.3	5.4	9.0
$\sigma_{C_{4-}}$ (%) [(a)]	7.0	6.6	6.4	8.1	1.1
$\sigma_{C_{5=}}$ (%) [(a)]	5.2	3.7	4.9	5.7	7.4
$\sigma_{C_{5-}}$ (%) [(a)]	4.1	3.5	3.7	4.6	0.4
$\sigma_{C_{6+}}$ (%) [(a)]	30.3	29.2	28.9	32.3	44.5

[(a)] CO-free values.

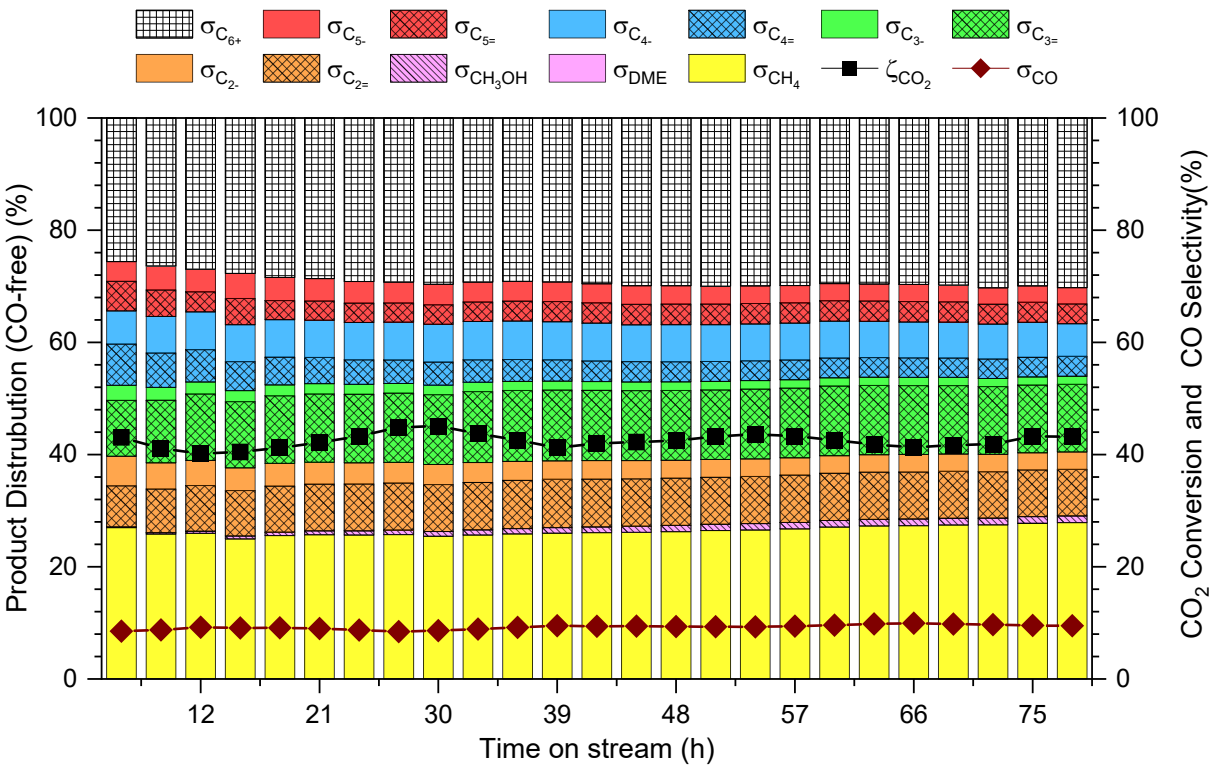

Figure S6. CO_2 conversion, CO selectivity and HCs selectivity (CO-free) during TOS for sample ACB-38. Reaction conditions: 7 NL·g$Fe_3O_4^{-1}$·h^{-1} ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na-Fe_3O_4, 2 g zeolite.

3.2. C_2-C_5 paraffin selectivity

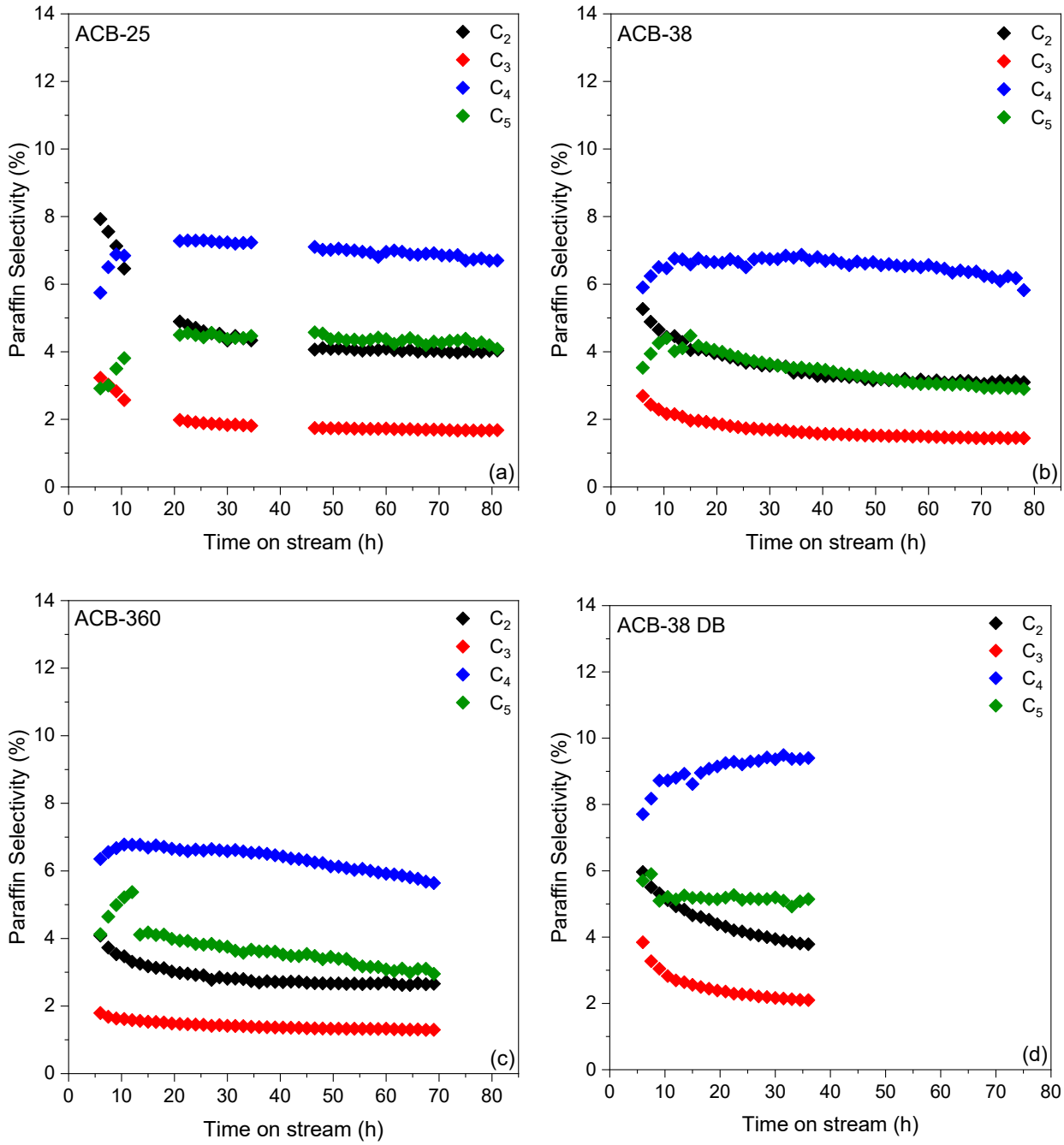

Figure S7. Profiles of the C_2-C_5 paraffin selectivity (CO-free) over time on stream: a) ACB-25, (b) ACB-38, (c) ACB-360 and (d) ACB-38_DB. Reaction conditions: 7 $NL \cdot gFe_3O_4^{-1} \cdot h^{-1}$ ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na-Fe_3O_4, 2 g zeolite.

4. Characterization of spent catalysts

4.1. TEM measurements

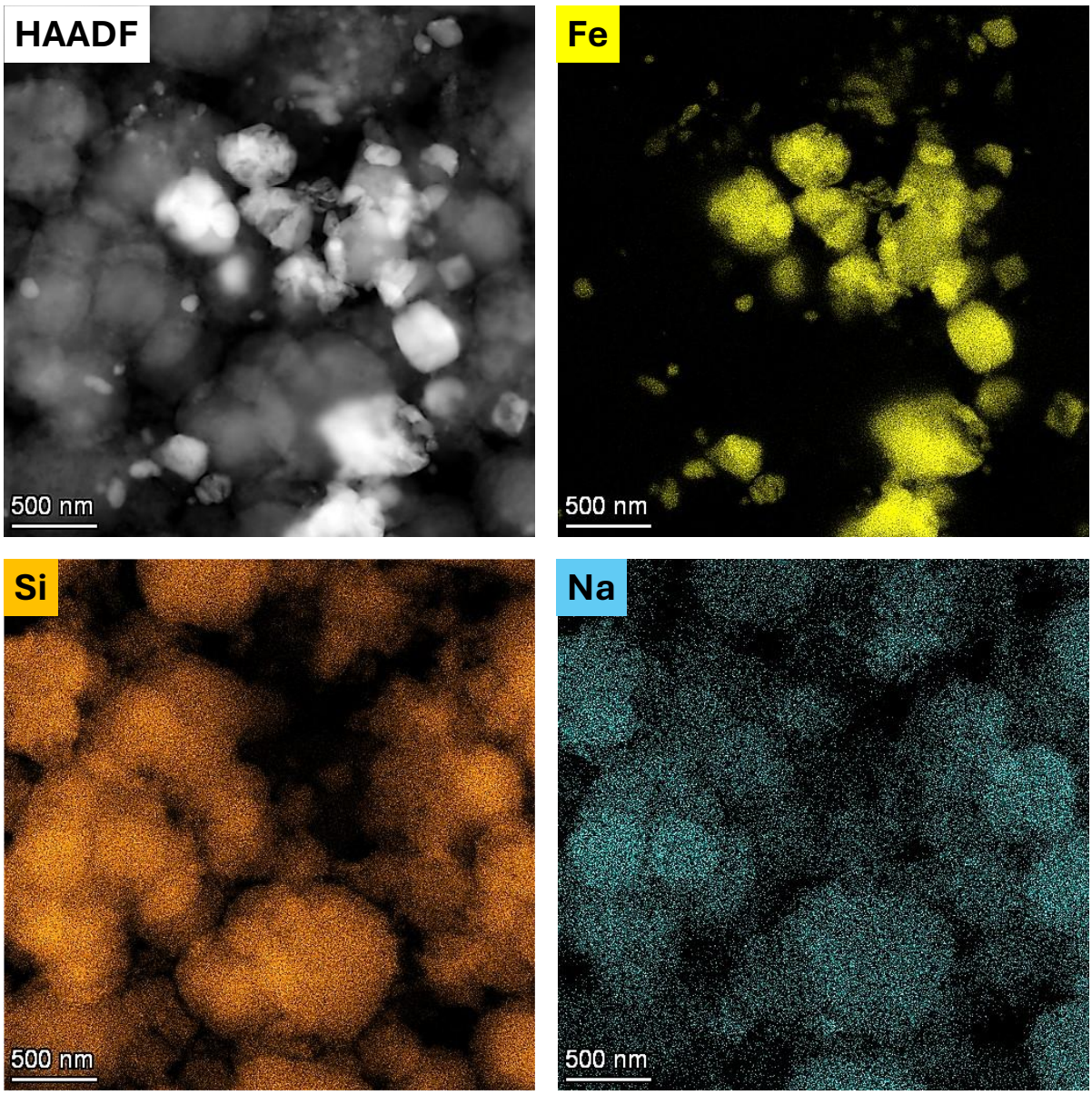

Figure S8. HAADF-STEM image and corresponding STEM-EDS elemental maps of the spent ACB-25 sample. The maps show the spatial distribution of Fe, Si and Na.

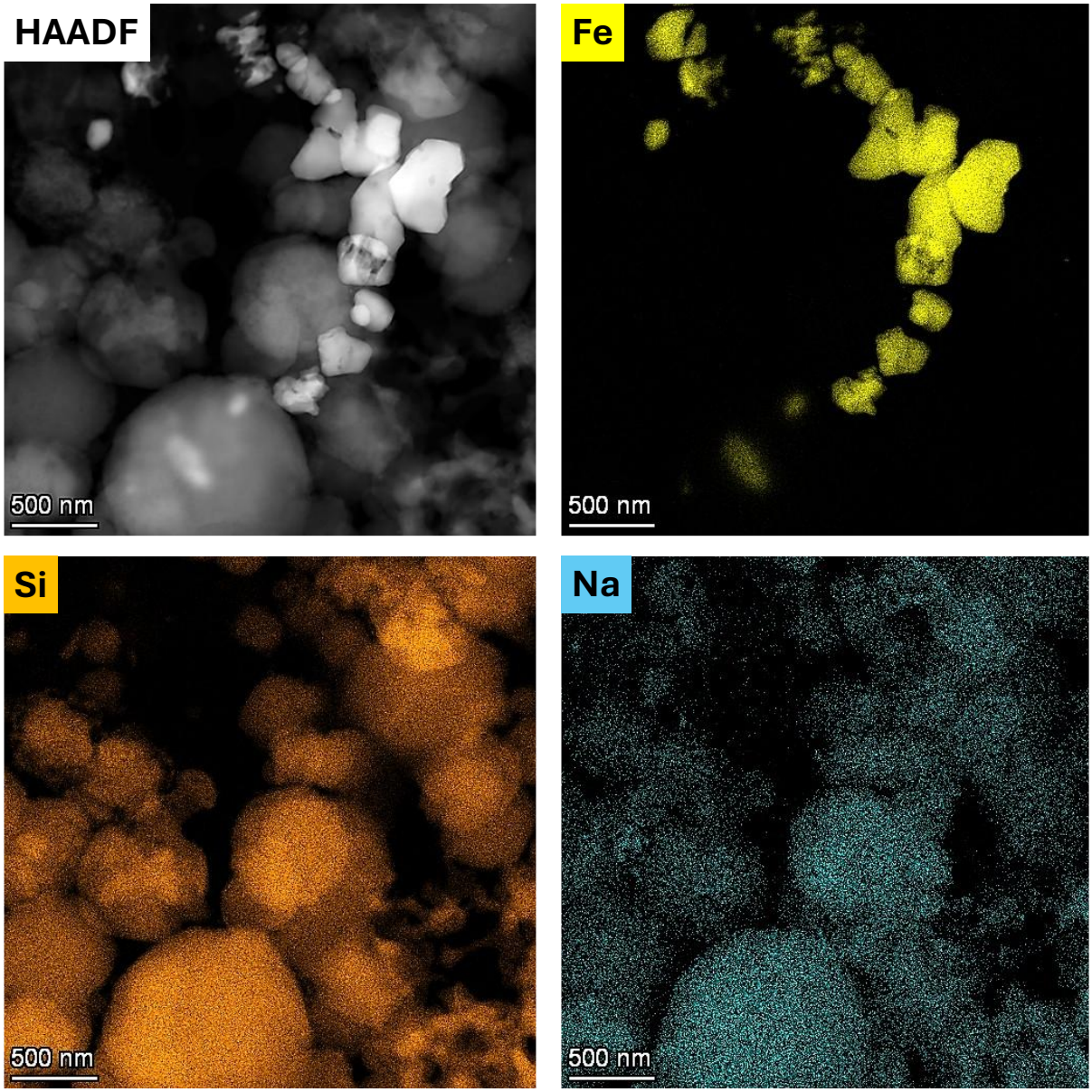

Figure S9. HAADF-STEM image and corresponding STEM-EDS elemental maps of the spent ACB-360 sample. The maps show the spatial distribution of Fe, Si and Na.

Table S4. Quantitative STEM-EDS analysis of zeolite-rich regions in the spent ACB samples.

Sample	Nominal Si/Al	Si/Al	Si /Al / Na	Na/Al	$mmol_{Na}/g_{zeolite}$
ACB-25	12.5	17.6	35.46 / 2.01 / 2.12	1.05	1.03
ACB-38	19	19.8	35.97 / 1.82 / 2.08	1.14	1.02
ACB-360	180	95.8	35.43 / 0.37 / 1.15	3.11	0.54
ACB-38_DB	19	20.2	36.42 / 1.80 / 0.41	0.22	0.20

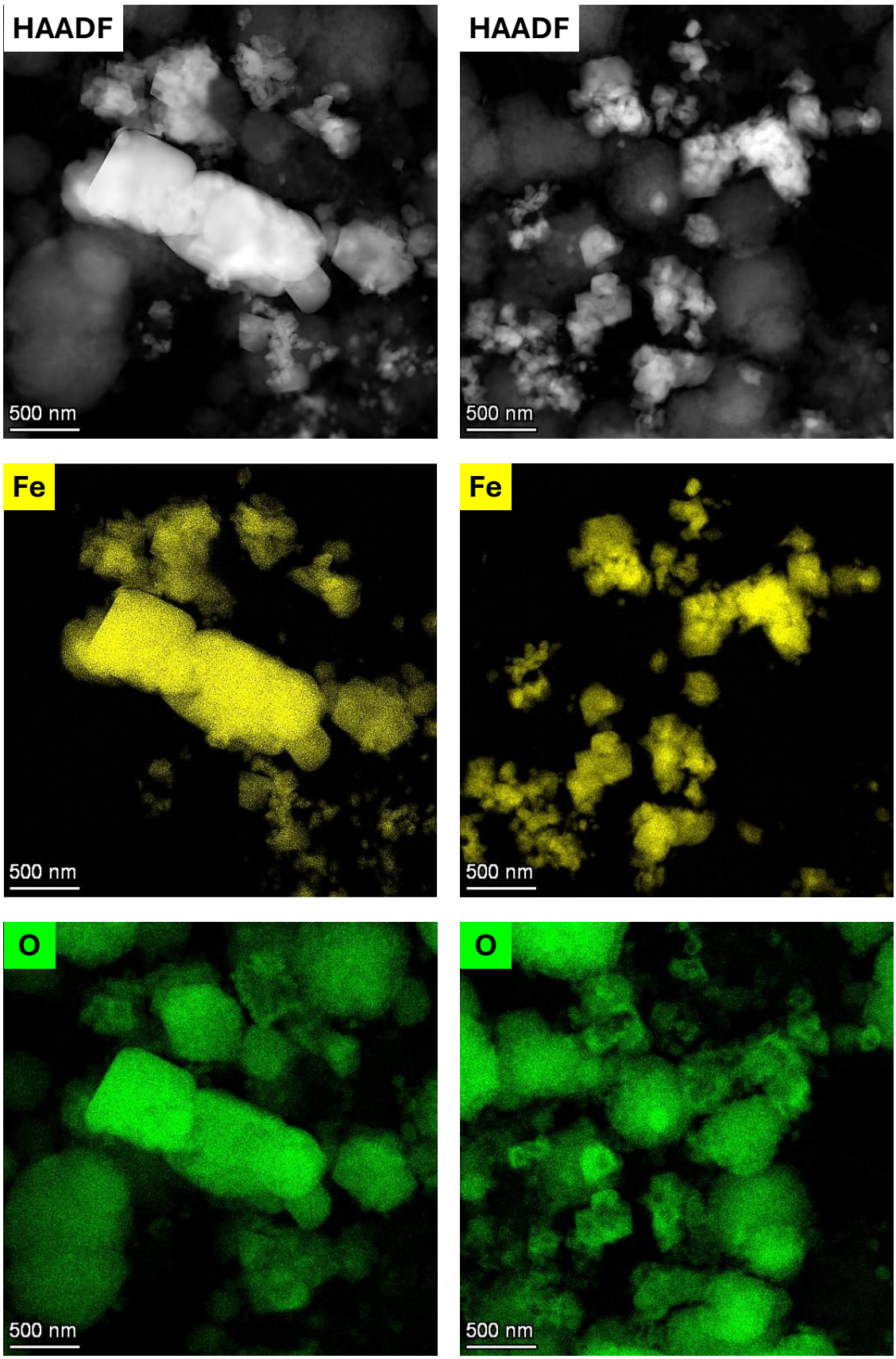

Figure S10. HAADF-STEM images and corresponding STEM-EDS elemental maps of two regions of the spent ACB-38_DB sample. The maps show the spatial distribution of Fe and O, focusing on the presence of iron oxide.

4.2. SEM measurements

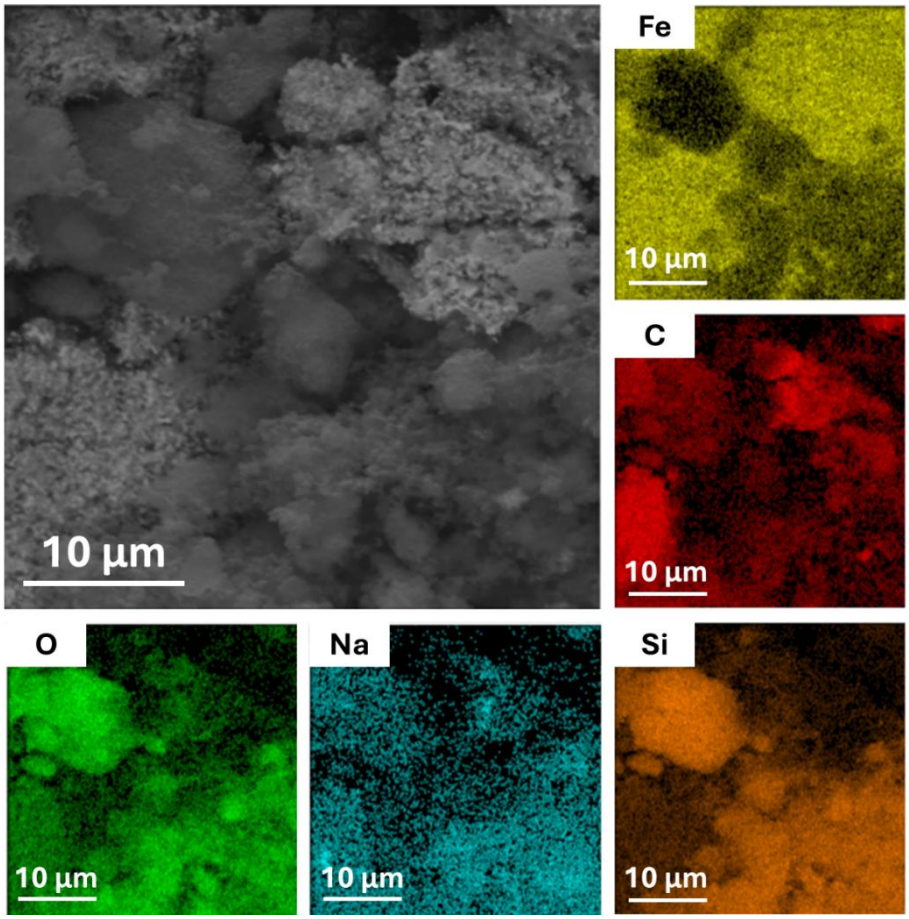

Figure S11. High-Resolution SEM image of test ACB-25 (magnification: 5.00 KX). SEM-EDS images of the main atoms.

Table S5. Atomic percentage of spent sample ACB-25 after SEM-EDS analysis.

Sample	Fe (at. %)	Si (at. %)	Al (at. %)	C (at. %)	O (at. %)	Na (at. %)
ACB-25	27.6	20.8	1.99	3.7	43.0	2.24

4.3. XRD measurements

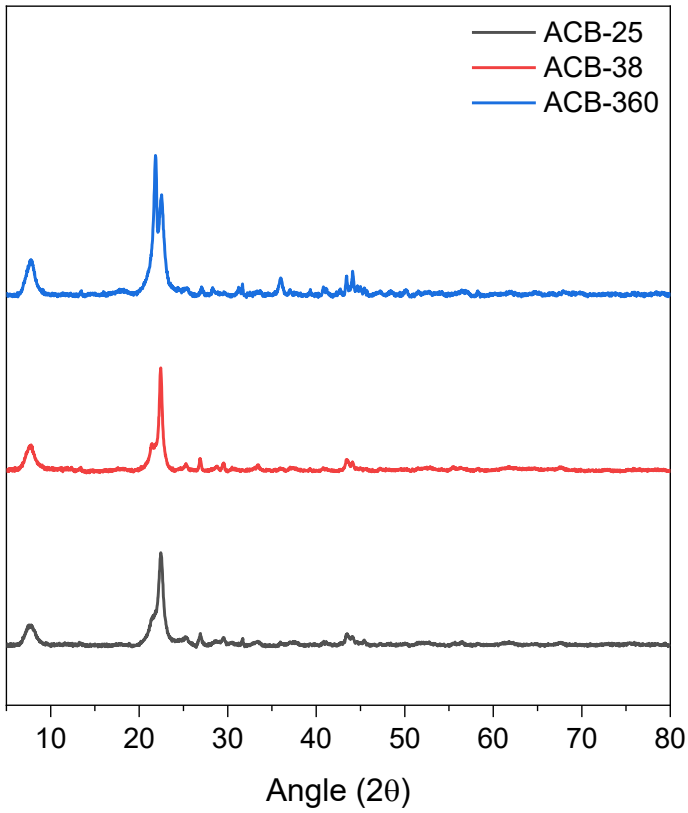

Figure S12. XRD profiles of the spent ACB samples over the 5°-80° 2θ range.

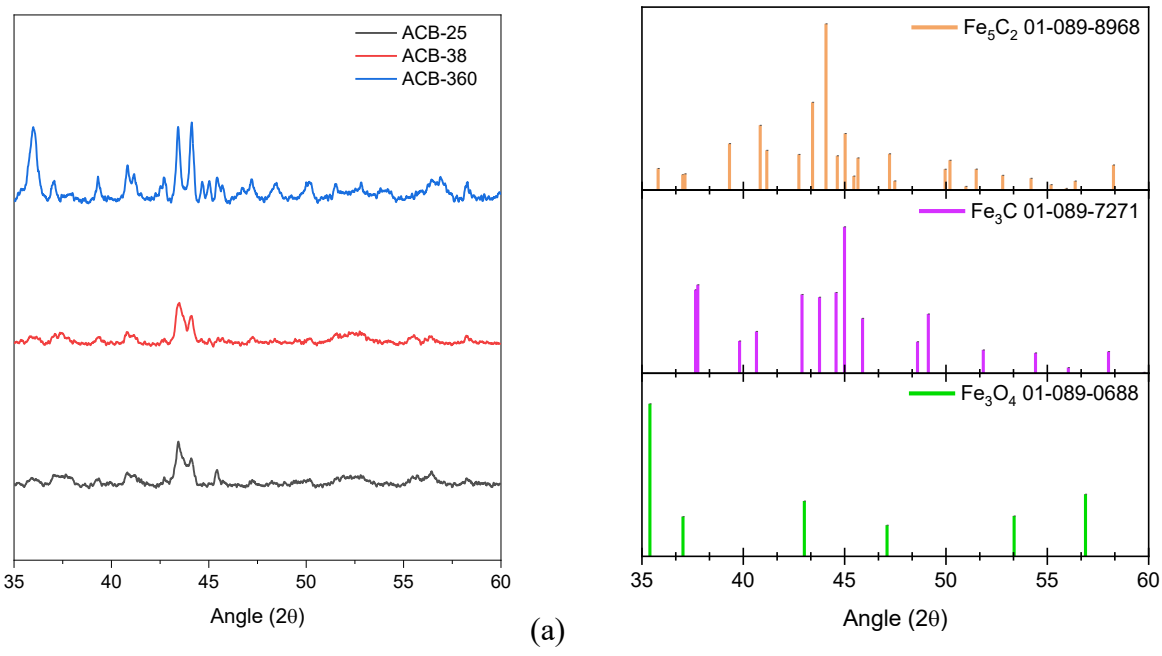

Figure S13. (a) Magnification of XRD profiles of spent ACB samples over the 35°-60° 2θ range, (b) reference diffraction patterns.

4.4. *Mössbauer spectroscopy results*

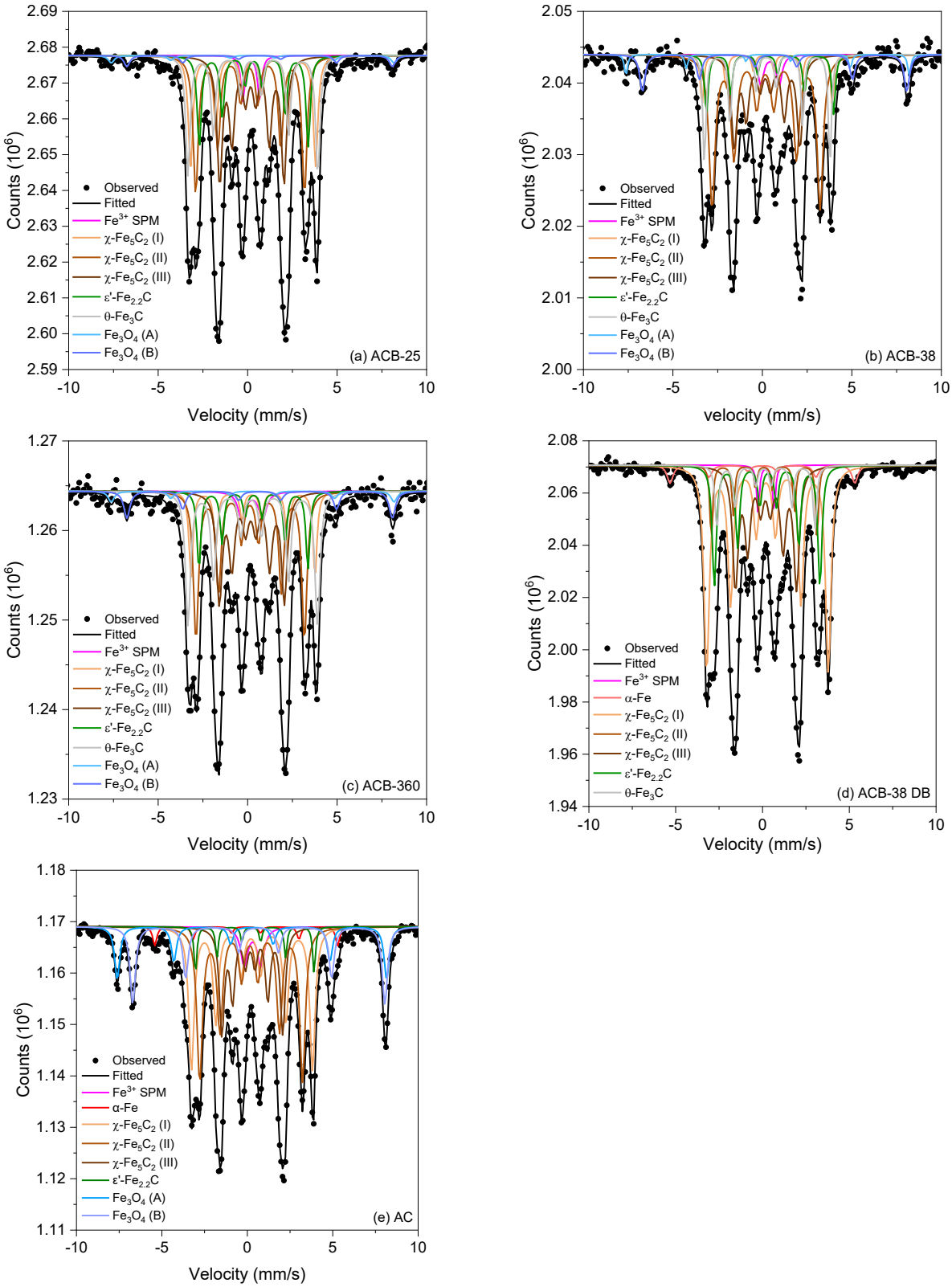

Figure S14. Room temperature Mössbauer spectra collected from spent samples: (a) ACB-25, (b) ACB_38, (c) ACB_360, (d) ACB-38 DB and (e) AC.

Table S6. Room temperature hyperfine parameters. δ is quoted relative to α-Fe foil. The errors are estimated as 0.02 mm/s for δ, Δ/ε and Γ_+ , 0.1 T for B and 5% for the relative area.

Sample	δ (mm/s)	ε/Δ (mm/s)	B (T)	Γ_+ (mm/s)	A (%)	Attributions	χ^2
ACB-25	0.20	0.93		0.13	3	Fe^{3+} SPM	1.37
	0.28	0.02	21.65	0.15	17	χ-Fe_2C_5 (I)	
	0.11	0.02	18.85	0.17	23	χ-Fe_2C_5 (II)	
	0.20	0.04	11.14	0.18	22	χ-Fe_2C_5 (III)	
	0.34	-0.001	18.86	0.14	13	ε'-$Fe_{2.2}C$	
	0.24*	0.05	22.5	0.14	18	θ-Fe_3C	
	0.28*	0*	49*	0.2*	2	Fe_3O_4 (Site A)	
	0.67*	0*	46*	0.2*	2	Fe_3O_4 (Site B)	
ACB-38	0.427	1.03	5000	0.19	3	Fe^{3+} SPM	0.64
	0.17	0.09	22.6	0.11	8	χ-Fe_2C_5 (I)	
	0.18	0.02	18.7	0.21	37	χ-Fe_2C_5 (II)	
	0.21	0.05	11.4	0.19	20	χ-Fe_2C_5 (III)	
	0.36	0.07	22.0	0.12	8	ε'-$Fe_{2.2}C$	
	0.24	0.03	21.8	0.10	14	θ-Fe_3C	
	0.31*	-0.02*	49.1*	0.10*	3	Fe_3O_4 (Site A)	
	0.72*	-0.03*	45.8*	0.17*	7	Fe_3O_4 (Site B)	
ACB-360	0.3	1.2		0.3	4	Fe^{3+} SPM	0.60
	0.27	0.04	21.5	0.13	11	χ-Fe_2C_5 (I)	
	0.13	0.01	18.79	0.17	25	χ-Fe_2C_5 (II)	
	0.20	0.03	11.3	0.19	21	χ-Fe_2C_5 (III)	
	0.33	-0.01	18.9	0.13	10	ε'-$Fe_{2.2}C$	
	0.24*	0.05	22.4	0.17	22	θ-Fe_3C	
	0.28*	0*	49*	0.2*	2	Fe_3O_4 (Site A)	
	0.67*	0*	46*	0.2*	5	Fe_3O_4 (Site B)	
ACB-38_DB	0.207	0.924		0.1	2	Fe^{3+} SPM	2.23
	0*	0*	33*	0.2*	4	α-Fe	
	0.2399	0.0485	21.727	0.1885	38	χ-Fe_2C_5 (I)	
	0.089	0.0071	18.898	0.097	7	χ-Fe_2C_5 (II)	
	0.1851	0.0170	10.919	0.197	23	χ-Fe_2C_5 (III)	
	0.298	-0.0310	18.866	0.144	17	ε'-$Fe_{2.2}C$	
	0.130	0.069	17.50	0.127	8	θ-Fe_3C	
AC	0.194	0.083	50.01	0.176	9	Fe_3O_4 (Site A)	1.04
	0.735	-0.019	46.53	0.299	19	Fe_3O_4 (Site B)	
	0.223	0.076	20.49	0.196	26	χ-Fe_2C_5 (I)	
	0.209	-0.003	17.37	0.180	26	χ-Fe_2C_5 (II)	
	0.134	0.006	9.45	0.193	17	χ-Fe_2C_5 (III)	
	0.33*	0*	21.02	0.114	4	ε'-$Fe_{2.2}C$	

* Refers to fixed parameters.

4.5. NH_3-TPD analysis results

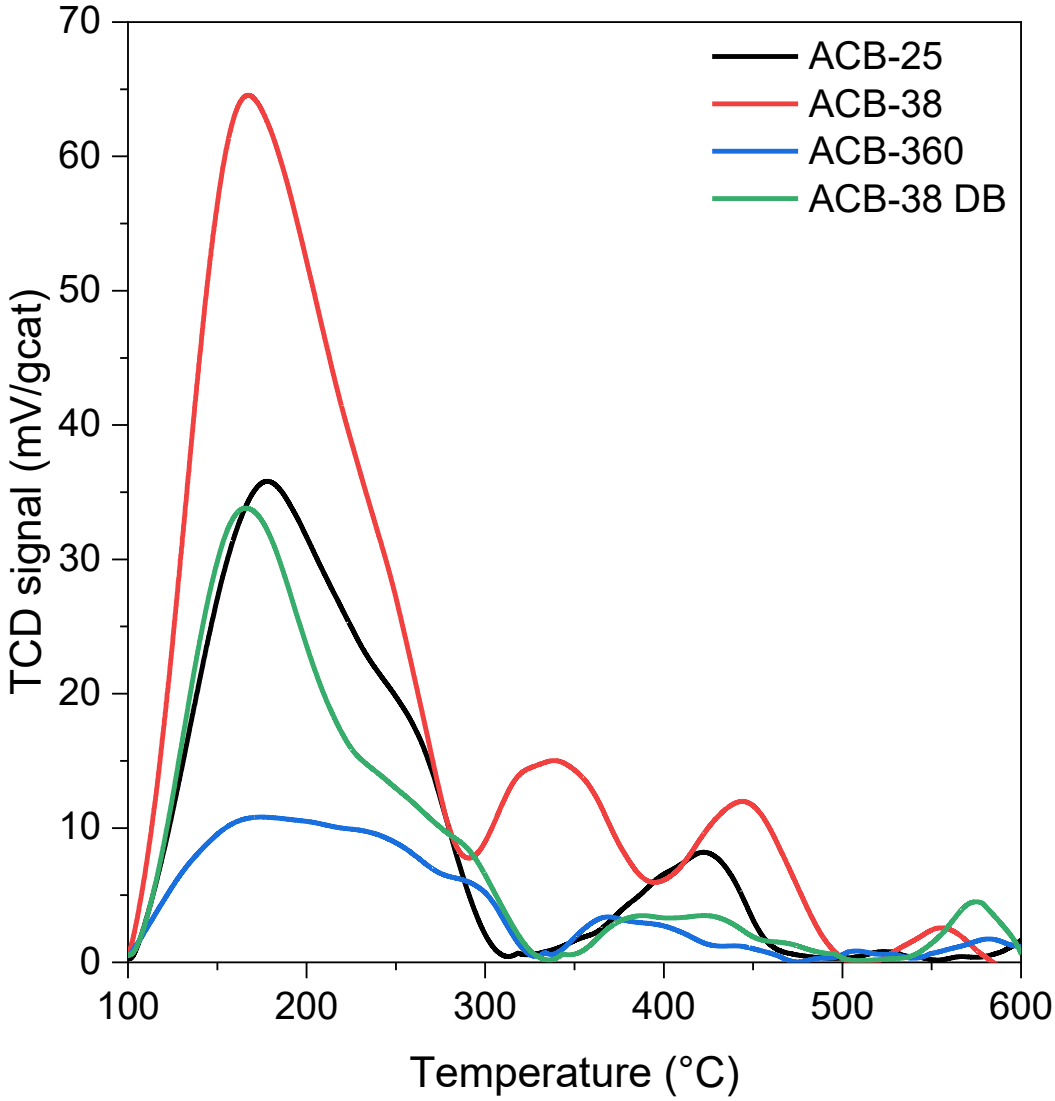

Figure S15. NH_3 temperature-programmed desorption (NH_3-TPD) profiles of the four spent samples: ACB-25, ACB-38, ACB-360, ACB-38_DB.

Table S7. NH_3-TPD results of spent samples.

Sample	Total acid sites (mmol·g^{-1})	W/S
ACB-25	0.033	6.5
ACB -38	0.062	3.3
ACB -360	0.015	4.5
ACB-38_DB	0.029	6.6

5. Liquid product analysis

5.1. DHA Results

Table S8. Mass percentage of HCs divided by class after DHA analysis. Reaction conditions: 7 $NL \cdot gFe_3O_4^{-1} \cdot h^{-1}$ ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe_3O_4, 2 g zeolite.

Sample	Unit	ACB-25[(a)]	ACB-38[(a)]	ACB-360[(a)]	ACB-38_DB	AC
N-paraffins	wt.%	7.23	6.60	5.12	7.94	6.32
Iso-paraffins	wt.%	19.29	18.80	16.66	18.13	12.05
Naphthenes	wt.%	8.45	8.52	8.90	6.89	3.36
N-olefins	wt.%	14.45	12.86	16.63	14.45	39.48
Iso-olefins	wt.%	27.73	26.34	22.92	23.55	10.52
Cyclo-olefins	wt.%	3.11	3.67	4.59	2.54	1.40
Di-olefins	wt.%	1.17	1.36	1.80	0.86	2.28
Aromatics	wt.%	12.86	14.65	12.83	16.66	16.05
Oxygenated	wt.%	0.02	1.20	3.34	0	0.02
Unknown	wt.%	5.70	5.99	7.22	8.97	8.52

[(a)]These samples are taken after 48 h of time on stream.

Table S9. Compounds present in the light oil with a wt.% > 0.5, classified by class and number of carbon atoms using DHA. Reaction conditions: 7 $NL \cdot gFe_3O_4^{-1} \cdot h^{-1}$ ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe_3O_4, 2 g zeolite.

Compound	Class	C atoms	ACB-25[(a)]	ACB-38[(a)]	ACB-360[(a)]	ACB-38_DB	AC
-	-	-	wt. %	wt. %	wt. %	wt. %	wt. %
c-2-butene	O	4	0.55	<0.5	0.64	0.53	<0.5
isobutene	O	4	0.55	<0.5	0.61	<0.5	1.04
t-2-butene	O	4	0.65	<0.5	0.79	0.62	<0.5
2-methyl-1-butene	iO	5	0.67	<0.5	<0.5	0.64	<0.5
2-methyl-2-butene	iO	5	2.44	1.60	1.98	2.40	<0.5
1-pentene	O	5	0.57	<0.5	0.54	<0.5	2.92
c-2-pentene	O	5	0.90	0.82	1.07	1.03	<0.5
isoPentane	iP	5	<0.5	<0.5	0.53	0.53	<0.5
pentane	P	5	0.52	<0.5	0.50	0.61	<0.5
t-2-pentene	O	5	1.65	1.62	2.07	2.01	<0.5
3-methyl-t-pentene-2	iO	6	1.77	1.50	<0.5	1.69	<0.5
3-methylcyclopentene	N	6	<0.5	<0.5	0.98	<0.5	<0.5
4-methyl-1-pentene	iO	6	<0.5	<0.5	<0.5	<0.5	0.70
c-3-methyl-2-pentene	iO	6	1.07	0.90	<0.5	1.03	<0.5
1-methylcyclopentene	N	6	0.50	0.67	0.65	<0.5	<0.5
2-methyl-1,4-pentadiene	dO	6	<0.5	0.77	1.03	<0.5	<0.5
2-methyl-2-pentene	iO	6	1.81	1.58	1.77	1.74	<0.5
1-hexene	O	6	0.72	0.51	0.73	0.69	6.09
c-2-hexene	O	6	1.02	1.07	1.08	1.01	<0.5
hexane	P	6	1.06	0.92	0.99	1.16	0.81

t-2-hexene	O	6	1.83	2.07	2.03	1.94	<0.5
t-3-hexene	O	6	0.82	<0.5	0.93	0.90	<0.5
3,4-dimethyl-2-pentene	iO	7	0.71	1.08	0.89	0.57	<0.5
2-methyl-1-hexene	iO	7	1.49	1.77	1.55	1.37	<0.5
2-methyl-2-hexene	iO	7	0.82	0.85	0.86	0.78	<0.5
2-methylhexane	iP	7	1.02	0.81	0.81	1.18	<0.5
3-methyl-1-hexene	iO	7	<0.5	<0.5	<0.5	<0.5	0.78
3-methyl-c-hexene-2	iO	7	2.43	2.65	<0.5	2.27	<0.5
3-methyl-t-2-hexene	iO	7	1.24	1.30	1.24	1.14	<0.5
3-methyl-t-hexene-3	iO	7	1.24	1.42	1.16	1.09	<0.5
3-methylhexane	iP	7	0.58	<0.5	<0.5	0.57	<0.5
4-methyl-2-hexene	iO	7	1.11	1.36	1.51	0.95	<0.5
1-heptene	O	7	0.59	<0.5	0.59	0.50	7.00
c-3-heptene	O	7	<0.5	<0.5	2.56	<0.5	<0.5
heptane	P	7	1.43	1.30	1.34	1.40	0.92
toluene	A	7	1.27	2.07	2.09	1.00	1.36
2,5-dimethyl-2-hexene	iO	8	0.59	0.54	<0.5	0.51	0.77
5,5-dimethyl-1,3-hexadiene	dO	8	<0.5	<0.5	<0.5	<0.5	0.62
c-1,4-dimethylcyclohexane	N	8	0.73	0.76	<0.5	0.55	<0.5
t-1,3-dimethylcyclohexane	N	8	<0.5	<0.5	1.78	<0.5	<0.5
2-methylheptane	iP	8	0.68	0.56	<0.5	0.72	<0.5
3-methyl-3-heptene	iO	8	<0.5	<0.5	1.71	<0.5	<0.5
4-methyl-3-heptene	iO	8	<0.5	0.51	<0.5	<0.5	<0.5
4-methylheptane	iP	8	0.73	0.98	1.04	0.63	0.62
1,2,3-trimethyl-cyclopentene	N	8	0.56	0.70	0.64	0.50	<0.5
2,3,4-trimethylpentane	iP	8	0.75	0.78	0.63	0.75	<0.5
1-octene	O	8	<0.5	<0.5	<0.5	<0.5	6.25
ethylbenzene	A	8	0.85	1.30	1.25	0.67	0.60
m-xylene	A	8	0.79	0.96	0.86	0.79	1.16
o-xylene	A	8	0.50	0.65	0.59	0.51	<0.5
octane	P	8	1.81	1.86	<0.5	1.72	0.89
t-Octene-3	O	8	1.63	1.96	<0.5	1.42	<0.5
3,3-dimethylheptene-1	iO	9	<0.5	<0.5	0.63	<0.5	<0.5
4-ethylheptane	iP	9	<0.5	<0.5	<0.5	<0.5	0.55
2-methyloctane	iP	9	0.56	0.55	<0.5	0.53	<0.5
2-methyloctene-2	iO	9	0.56	0.61	0.49	<0.5	<0.5
3-methyloctane	iP	9	0.57	0.58	<0.5	0.53	<0.5
1,2,4-trimethylbenzene	A	9	0.65	0.58	<0.5	0.74	<0.5
1-ethyl-3-methylbenzene	A	9	0.62	0.75	0.62	0.58	<0.5
1-nonene	O	9	<0.5	0.56	0.51	<0.5	4.61
c-3-nonene	O	9	0.56	0.62	0.51	<0.5	<0.5
n-propylbenzene	A	9	0.50	0.68	0.61	<0.5	<0.5
nonane	P	9	0.92	0.84	0.84	0.85	0.71
3-methylnonane	iP	10	<0.5	0.52	0.50	<0.5	<0.5
1-decene	O	10	<0.5	<0.5	<0.5	<0.5	3.44
decane	P	10	0.65	0.60	0.56	0.61	0.52
5-methyl-decane	iP	11	<0.5	<0.5	<0.5	<0.5	0.52
Dodecene-1	O	12	<0.5	<0.5	<0.5	<0.5	1.64
1-tridecene	O	13	<0.5	<0.5	<0.5	<0.5	1.09
1-tetradecene	O	14	<0.5	<0.5	<0.5	<0.5	0.67

[(a)]These samples are taken after 48 h of time on stream.

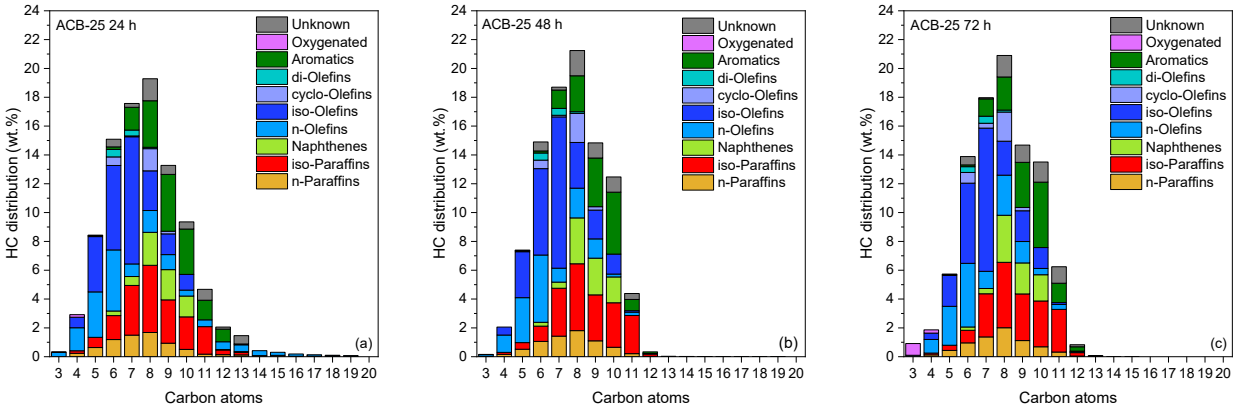

Figure S16. Effect of time on the distribution and classes of hydrocarbons for sample ACB-25: (a) 24 h, (b) 48 h and (c) 72 h. Reaction conditions: 7 NL·g$Fe_3O_4^{-1}$·h^{-1} ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe_3O_4, 2 g zeolite.

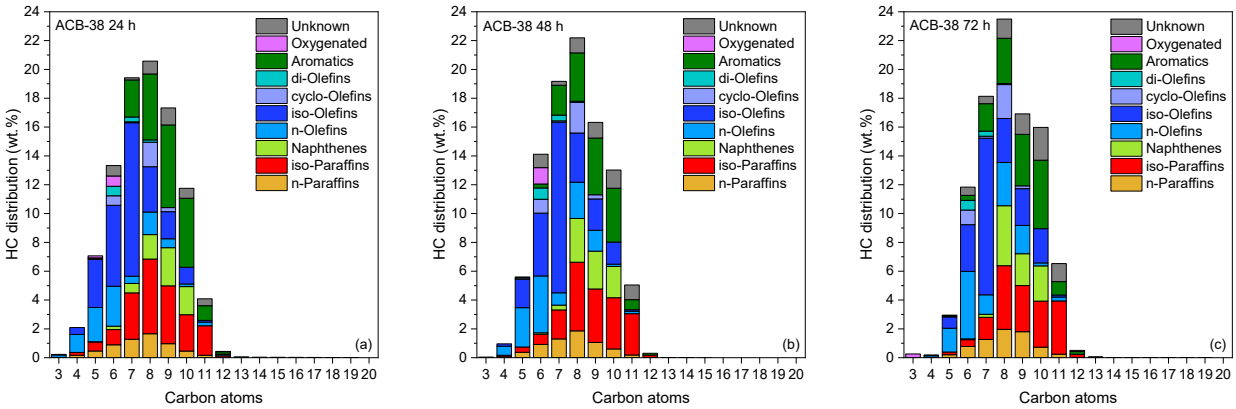

Figure S17. Effect of time on the distribution and classes of hydrocarbons for sample ACB-38: (a) 24 h, (b) 48 h and (c) 72 h. Reaction conditions: 7 NL·g$Fe_3O_4^{-1}$·h^{-1} ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe_3O_4, 2 g zeolite.

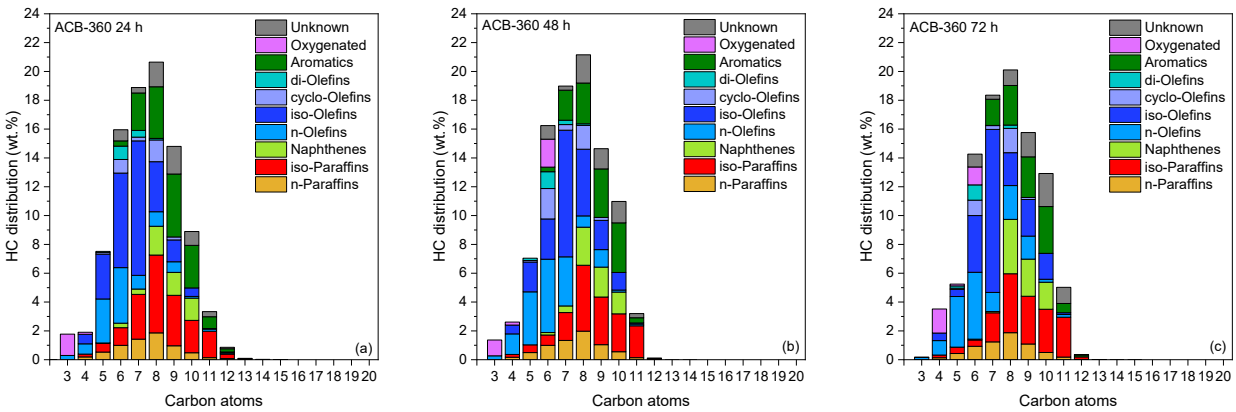

Figure S18. Effect of time on the distribution and classes of hydrocarbons for sample ACB-360: (a) 24 h, (b) 48 h and (c) 72 h. Reaction conditions: 7 NL·g$Fe_3O_4^{-1}$·h^{-1} ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe_3O_4, 2 g zeolite.

6.1. *GC-MS analysis results*

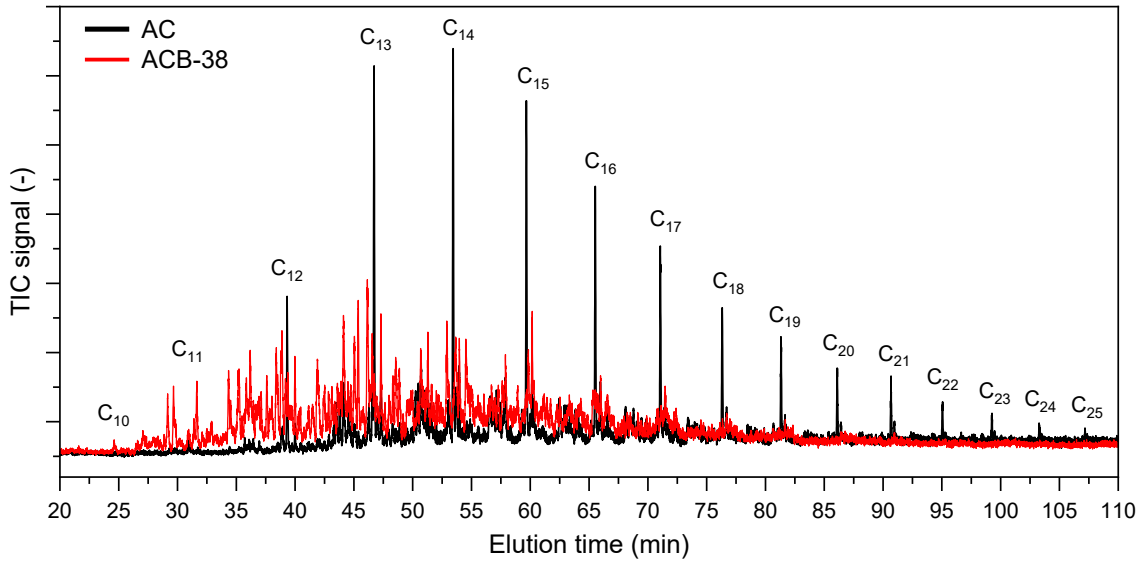

Figure S19. Chromatograms obtained from the GC-MS analysis of heavy oil, comparing results with and without zeolite. Reaction conditions: 7 NL·g$Fe_3O_4^{-1}$·h^{-1} ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe_3O_4, 2 g zeolite.

6.2. *HPLC analysis results*

Table S10. Oxygenated compounds in the aqueous phase collected from the hot trap, as determined by HPLC. Reaction conditions: 7 NL·g$Fe_3O_4^{-1}$·h^{-1} ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe_3O_4, 2 g zeolite.

Sample	AC	ACB-25	ACB-38	ACB-360	ACB-38_DB
Compound	mg/L	mg/L	mg/L	mg/L	mg/L
Formic acid	-	29872	27454	25923	37784
Acetic acid	11871	17942	9160	10086	18983
1,2-Propandiol	1899	1195	1763	1885	1724
Propanoic acid	2292	2903	6253	1459	2728
Methanol	110	0	0	0	0
Ethanol	3626	1800	3091	2799	2035
2-Propanol	202	121	225	270	139
1-Propanol	149	0	0	0	0
Diethyl ether	861	566	1039	1007	715
2-Butanol	0	0	0	0	0
Phenol	57	27	34	72	20

Table S11. Oxygenated compounds in the aqueous phase collected from the cold trap, as determined by HPLC. Reaction conditions: 7 $NL \cdot gFe_3O_4^{-1} \cdot h^{-1}$ ($H_2/CO_2/N_2$ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe_3O_4, 2 g zeolite.

Sample	AC	ACB-25	ACB-38	ACB-360	ACB-38_DB
Compound	mg/L	mg/L	mg/L	mg/L	mg/L
Formic acid	-	7078	7889	2676	2279
Acetic acid	7721	11207	18530	15673	10924
1,2-Propandiol	1844	2637	3780	2731	1450
Propanoic acid	2441	2289	2259	3197	1085
Methanol	2524	4686	8120	3669	176
Ethanol	117522	120330	131851	177121	34894
2-Propanol	1194	1134	2293	994	648
1-Propanol	9137	4597	3965	7011	719
Diethyl ether	1999	1514	1330	1973	1394
2-Butanol	247	253	630	201	141
Phenol	164	114	111	197	24