Catalytic Hydroconversion of Derivates from Shaerhu Subbituminous Coal over a Ni-Based MOFs-Derived Carbon Matrix Superacid Catalyst

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1. Experimental

1.1. Materials

SSBC was collected from Shaerhu Coal Mine, Xinjiang Uygur Autonomous Region, China, and pulverized to pass through a 200-mesh sieve followed by dessication in a vacuum oven at 80 °C for 48 h. Proximate and ultimate analyses of SSBC was shown in Table S1. All the reagents used in the experiments are of analytical grade. *N,N*-dimethylformamide, *n*-hexane, carbon disulfideand and acetone were purchased from Xilong Chemical Co, Ltd, Guangdong, China and were distillated before use. $Ni(NO_3)_2.6H_2O$, TFMSA, trimesic acid, BON and BOB were purchased from Shanghai Anagi Chemical Reagent Co., Ltd., Shanghai, China.

1.2. Catalyst preparation

NOFW was synthesized through a conventional hydrothermal approach. Typically, 0.01 mol $Ni(NO_3)_2 \cdot 6H_2O$ and 0.01 mol trimesic acid were co-dissolved in 80 mL *N*,*N*-dimethylformamide (DMF) with ultrasonication assist for 0.5 h. The resulting homogeneous solution was transferred to a 100 mL Teflon-lined autoclave and hydrothermally treated at 150 °C for 4 h followed by filtration. The filter cake was washed with ethanol and vacuum-dried at 80 °C for 24 h to obtain green powder

NOFW. The NOFW was pyrolyzed and carbonized in a tubular furnace with ceaseless N_2 flow to afford the CNOFW-T at varying calcination temperatures (T = 400-700 °C) for 1.5 h.

TFMSA/CNOFW was prepared by an impregnation method. In brief, 1 g CNOFW was impregnated with 5 mL TFMSA in a 25 mL three-neck flask under N_2 atmosphere. The resulting mixture was mechanically stirred at 30 °C for 12 h and subsequently filtrated. The black filter cake was washed 3 times with ethanol and dried in vacuum to afford TFMSA/CNOFW.

1.3. SSBC pretreatment

About 3 g SSBC was mixed with 100 mL CCl_4 under ultrasonication, and the mixture was then transferred to a separatory funnel to stand for 0.5 h. Following filtration, the upper light coal sample was dried under vacuum at 80 °C for 24 h. For exhaustive extraction, the dried coal sample (2 g) was treated with 150 mL isometric carbon disulfide/acetone mixed solvent under ultrasonication at room temperature to afford extraction residue (ER).

Table S1
Proximate and ultimate analyses of SSBC.

Sample	Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$
	M_{ad}	A_d	V_{daf}	C	H	N	O_{diff}	
SSBC	12.4	5.1	36.7	69.8	4.7	0.6	24.8	0.1
ER	12.6	5.6	35.4	67.9	4.3	0.5	27.2	0.1

daf: dried and ash-free basis; diff: by difference.

1.4. NCHC and CHC of ER

In a typical procedure, *n*-hexane (20 mL), ER (1 g), and TFMSA/CNOFW (0 or 0.2 g) were added into an autoclave. The system was purged with H_2 and pressurized to 1 MPa initial hydrogen pressure (IHP). The reaction was conducted at 300 °C and maintained for 4 h, followed by cooling to room temperature in a water bath. The resulting mixture was thoroughly extracted with IMACDSMS under ultrasonication, filtered, and further extracted with *n*-hexane to obtain soluble portions from NCHC and CHC of ER, denoted as SP_{NCHC} and SP_{CHC}, respectively, and the insoluble portions as ISP_{NCHC}

and ISP_{CHC}.

1.5. Catalyst characterization

TG analysis was conducted with NETZSCH STA449F5 TG analyzer. The specific surface area (SSA) and pore size distribution of catalysts were measured by Autosorb-1-MP type physisorption at -196 ^{o}C. The X-ray diffraction (XRD) measurement was carried out with a Bruker Advance D8 XRD equipped with a Cu Kα source by scanning from 10^{o} to 80 ^{o} at a rate of 0.2 s step^{-1}. Scanning electron microscopic images (SEMIs) and high-resolution transmission electron microscope images (HRTEMIs) were taken on ZEISS Sigma 300 microscope and FEI Tecnai G2 F20 transmission electron microscope. X-ray photoelectron spectrum (XRPES) was recorded on a Thermo Fisher Scientific Kα 1063 spectrophotometer with the Al Kα radiation. Ni content was determined with a laser ablation inductively coupled plasma mass spectrometer (LA/ICP-MS). NH_3 temperature programmed desorption (NH_3-TPD) and pyridine infrared spectrum were determined with a TP-5000II type multi-function adsorption instrument. Infrared spectral analysis was analyzed with a Bruker Vertex 80 v Fourier transform infrared (FTIR) spectrometer. TPR of Ni/SiO_2 with H_2 was conducted with an automated chemisorption flow analyzer with a 5% H_2/Ar mixture at a heating rate of 5 ^{o}C min^{-1}. Magnetic hysteresis loop was carried out on a LakeShore 7404 vibrating sample magnetometer.

1.6. Sample analyses

The BON, SP_{NCHC} and SP_{CHC} were analyzed with an Agilent 7890/5975 gas chromatography/mass spectrometer (GC/MS) which is equipped with a HP-5MS non-polar capillary column. The oven temperature was heated from 60 to 300 ^{o}C at a heating rate of 5 ^{o}C·min^{-1} and kept at 300 ^{o}C for 10 min. SP_{NCHC} and SP_{CHC} were analyzed with FTIR and quadrupole exactive orbitrap mass spectrometer (QPEOTMS) with atmospheric-pressure chemical ionization in positive-ion mode. To

ensure the accuracy of the data, each experiment was repeated at least three times.

Table S2
SSAs, TPVs, and APDs of the samples along with Ni content in NOFW and CNOFW-T.

Sample	SSA (m^2 g^{-1})	TPV (cm^3 g^{-1})	APD (nm)	Ni content (wt%)
NOFW	206.7	0.08	2.9	14.3
CNOFW-400	109.9	0.20	1.4	39.9
CNOFW-500	130.9	0.20	1.4	48.1
CNOFW-600	145.1	0.27	1.5	66.7
CNOFW-700	99.1	0.17	1.8	30.8
TFMSA/CNOFW	97.8	0.22	3.1	

* Measured with LA/ICP-MS.

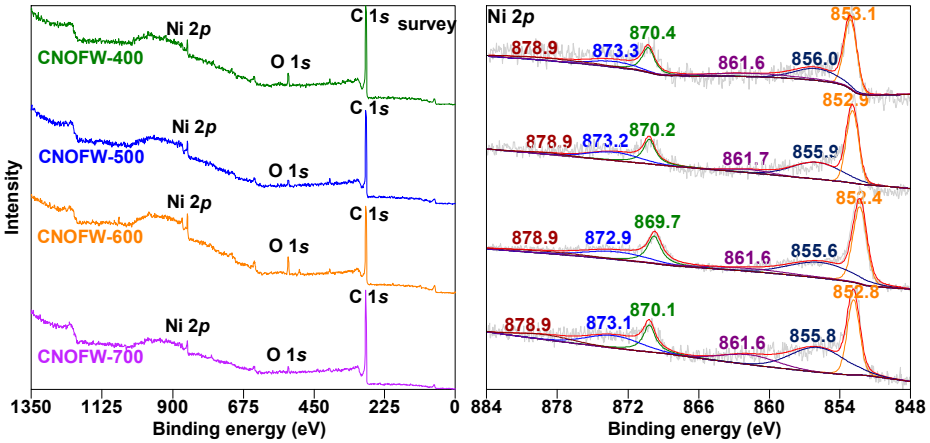

Fig. S1. XPS of CNOFW-T.

Table S3
Qualitative and quantitative analysis of surface element Ni of CNOFW-T.

CNOFW-T	Binding energy (eV)	Abundance (%)	CNOFW-T	Binding energy (eV)	Abundance (%)
400	853.1	1.22	600	852.4	3.94
500	852.9	1.30	700	852.8	2.59

Table S4
Qualitative and quantitative analysis of surface elements of TFMSA/CNOFW.

Element	Binding energy (eV)	Abundance (%)	Element	Binding energy (eV)	Abundance (%)
Ni 2*p*	856.1	3.5	O 1*s*	532.1	9.2
C 1*s*	284.9	79.0	F 1*s*	688.6	3.4
S 2*p*	169.1	4.9			

Table S5
Catalytic hydrocracking of other model compounds over TFMSA/CNOFW.

Substrate	Reaction conditions		Conversion (%)	Selectivity (%)			
	Temperature (°C)	IHP (MPa)		Toluene	Ethylbenzene	Phenol	Others
BOB	120	1	71.5	49.3		17.8	4.4
BOB	140	1	100	63.6		35.1	1.3
POB	160	1	3.1		2.2	0.9	
POB	180	2	74.9		49.6	25.3	
OBMDB	160	2	13.9	11.1			
OBMDB	180	2	95.4	75.4			20

Substrate 100 mg, TFMSA/CNOFW 30 mg, *n*-hexane 20 mL, 2h

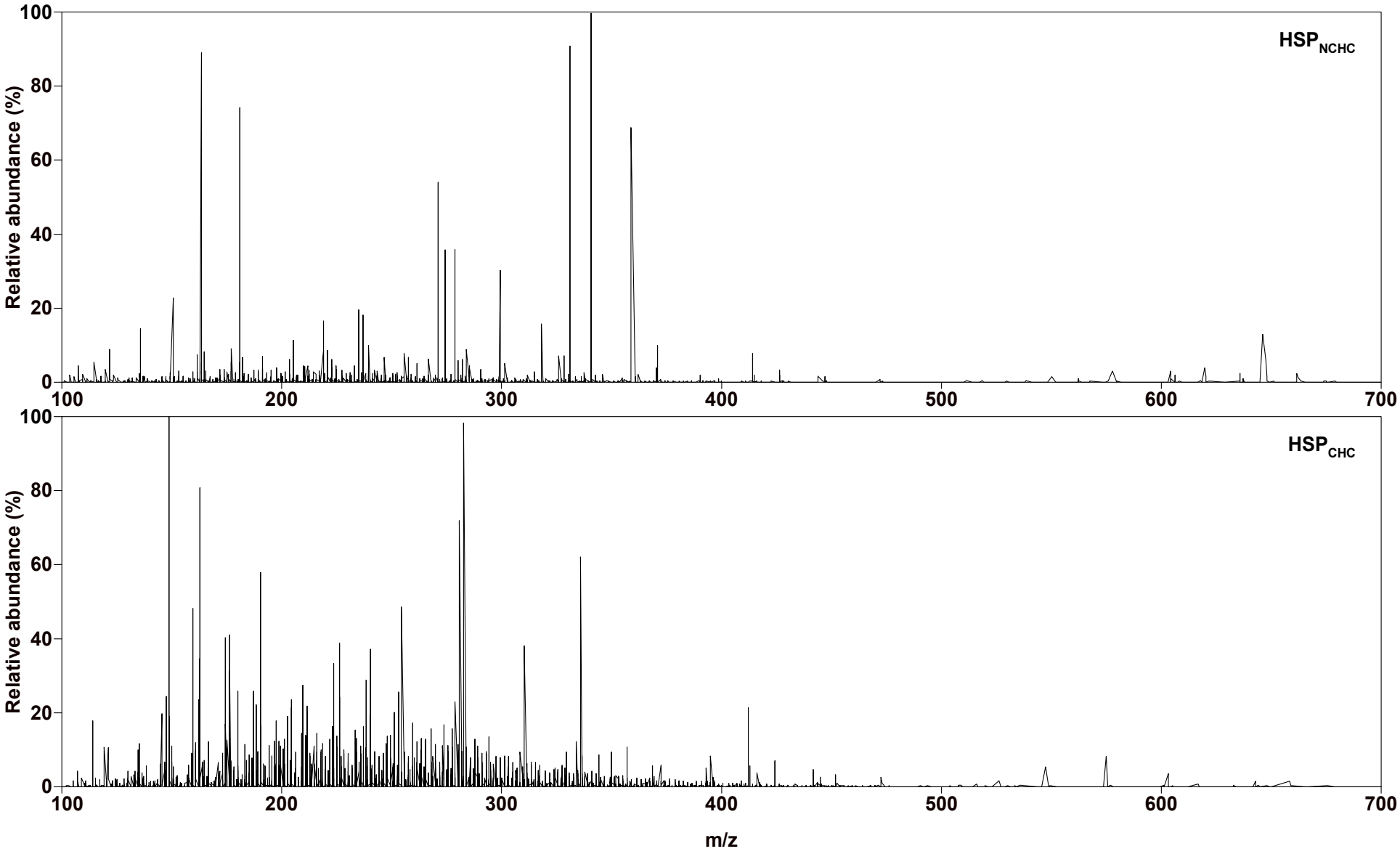

Fig. S2. Mass spectra of HSP_{NCHC} and HSP_{CHC} detected with QPEOTMS.

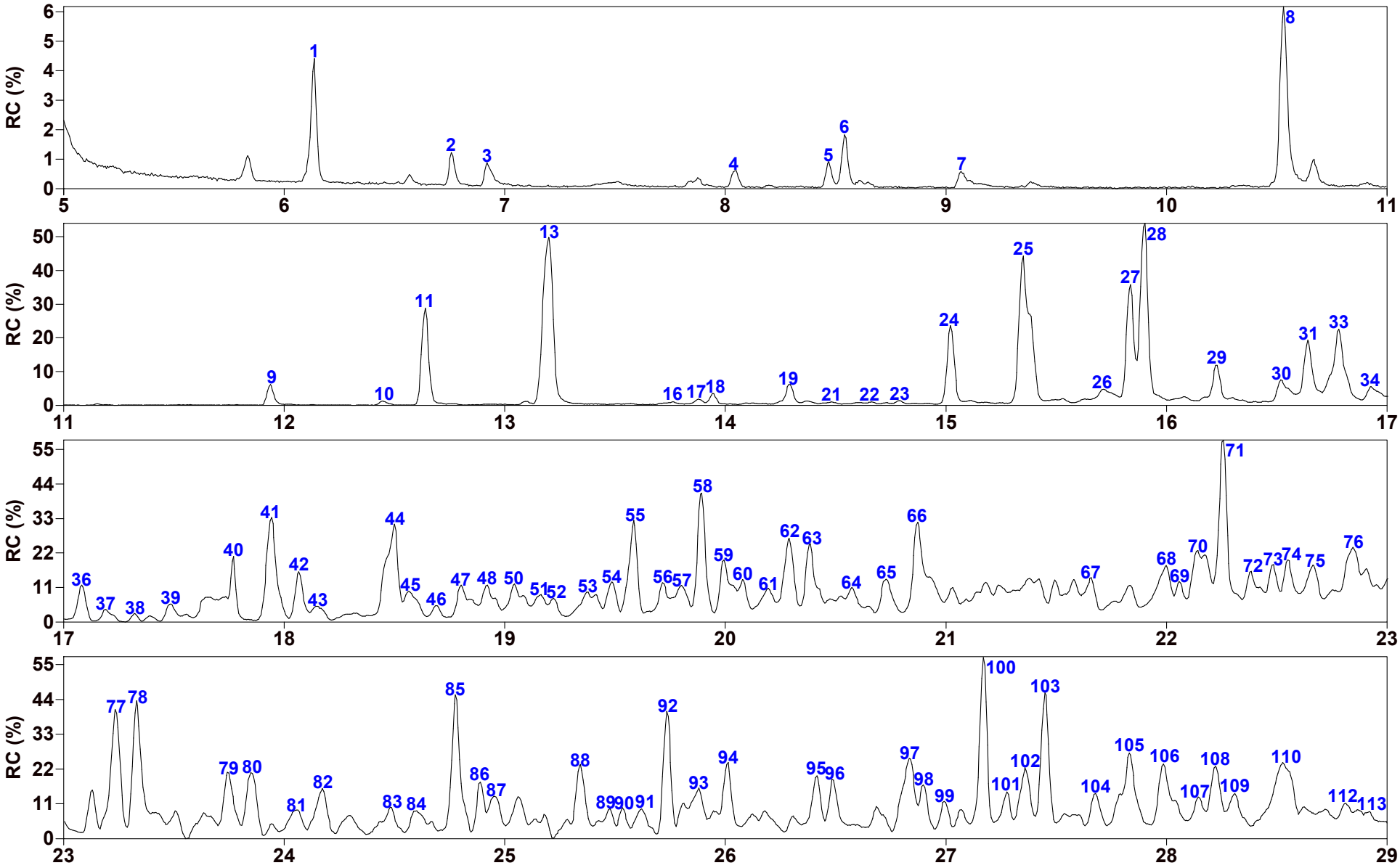

Fig. S3. Total ion chromatogram of SP_{NCHC}.

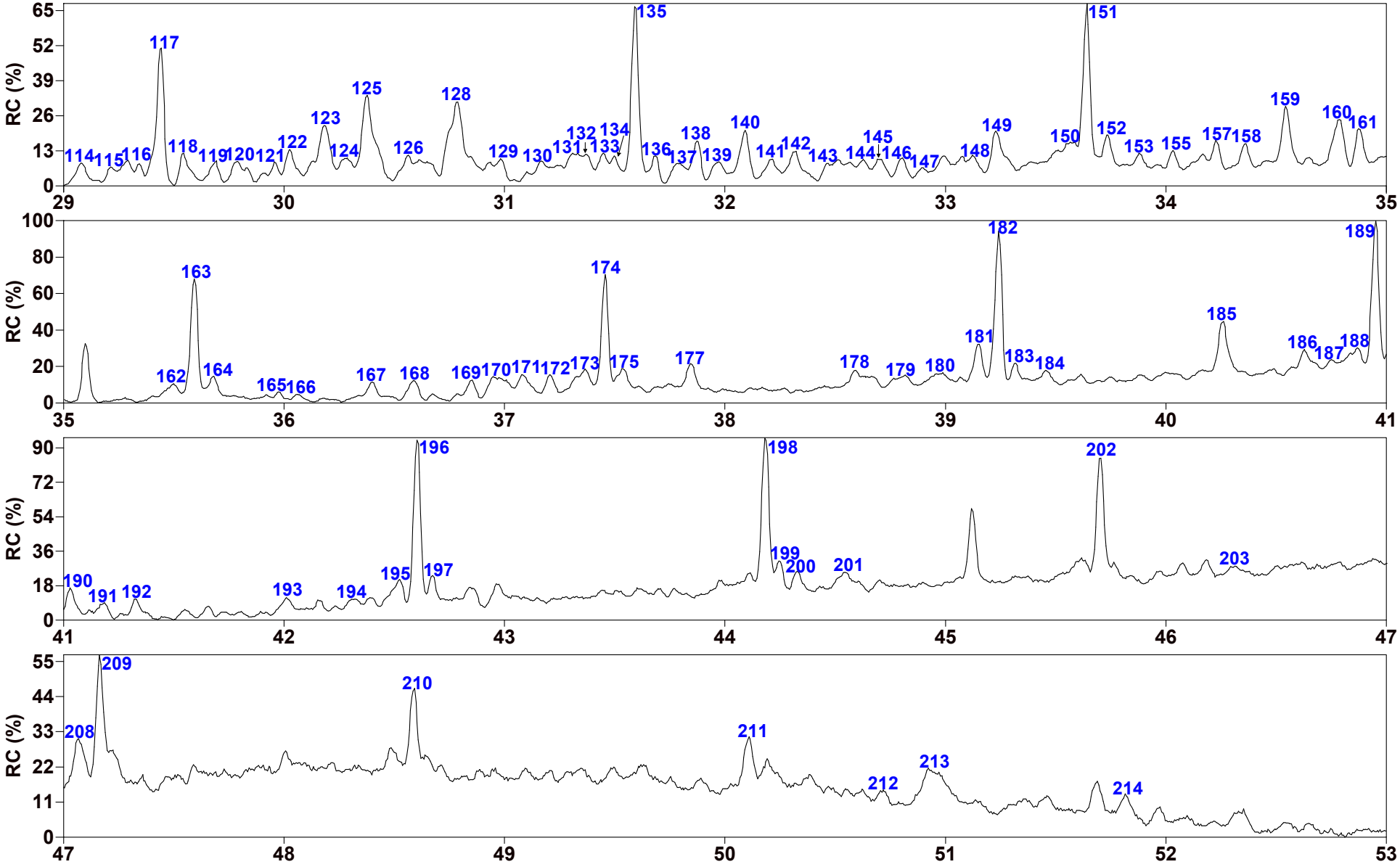

Fig. S3. Total ion chromatogram of SP_{NCHC} (continued).

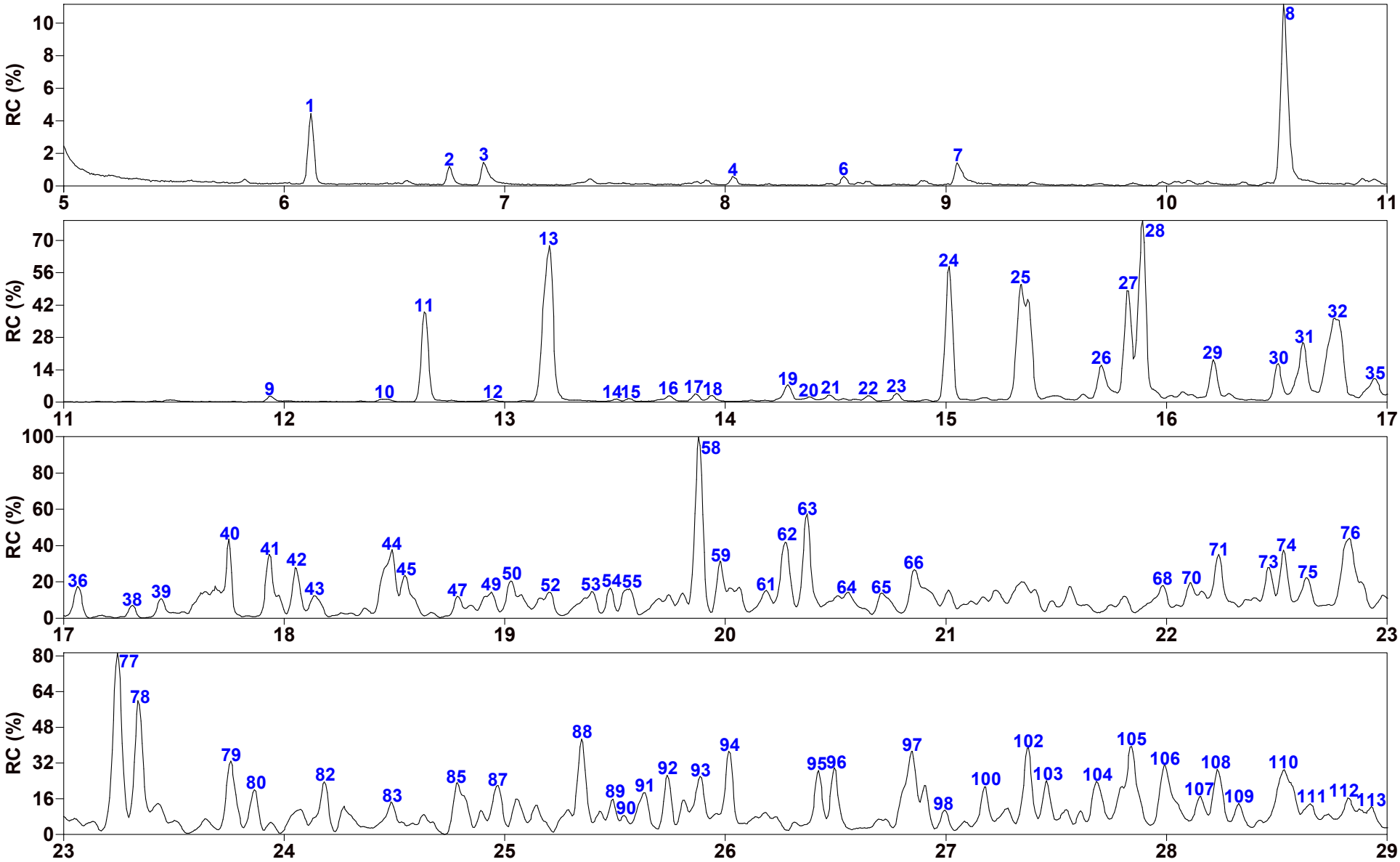

Fig. S4 Total ion chromatogram of SP_{CHC}.

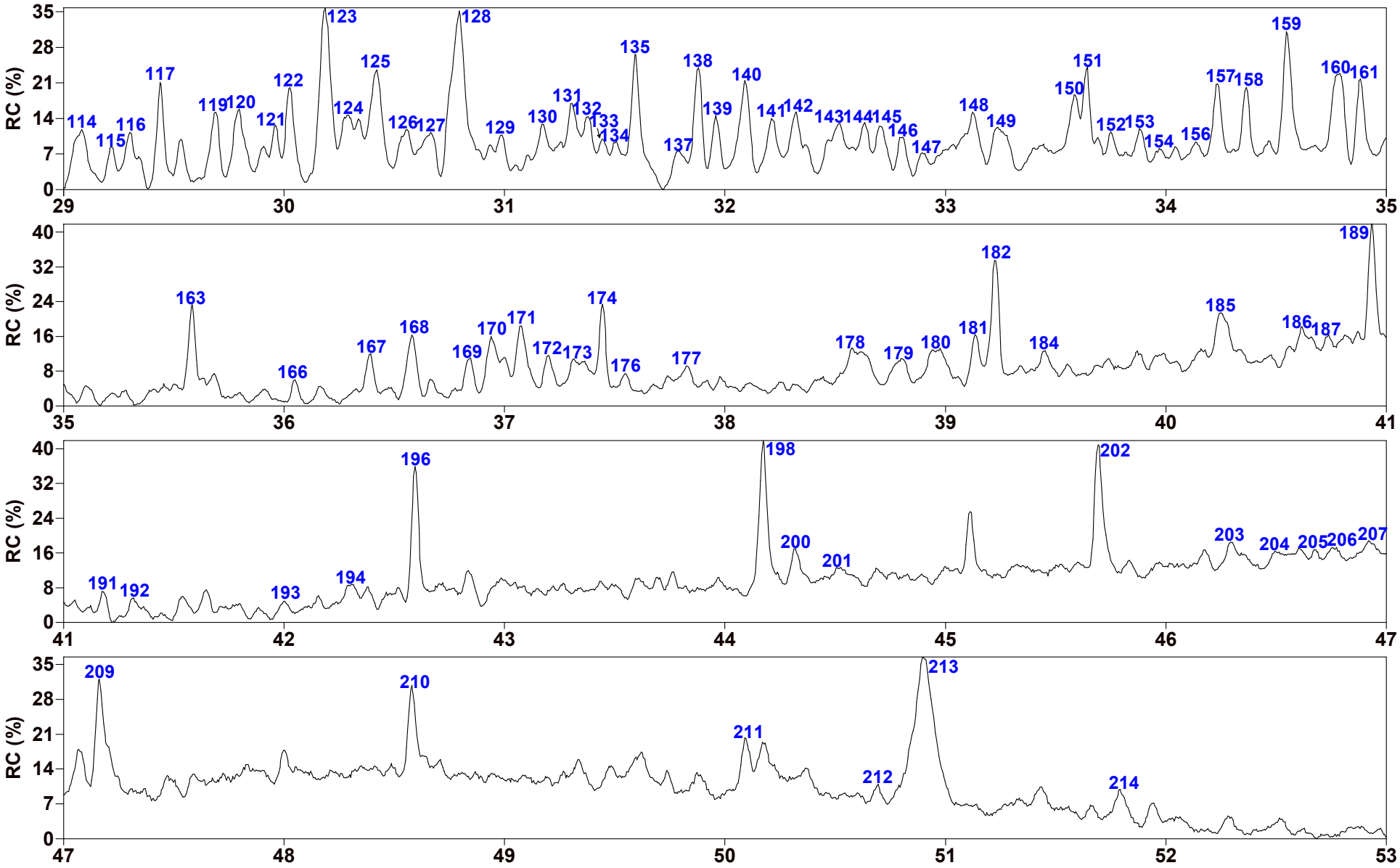

Fig. S4. Total ion chromatogram of SP_{CHC} (continued).

Table S6
NAs detected in SP_{NCHC} and SP_{CHC}.

Peak	NA	RC		Peak	NA	RC		Peak	NA	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
18	Undecane	0.08	0.06	**135**	Octadecane	1.93	0.84	**198**	Pentacosane	2.16	1.13
33	Dodecane	0.95	0	**151**	Nonadecane	1.51	0.28	**202**	Hexacosane	1.81	1.09
55	Tridecane	1.05	0.60	**163**	Eicosane	1.89	0.49	**209**	Heptacosane	0.99	1.01
71	Tetradecane	1.47	0.76	**174**	Heneicosane	1.71	0.47	**210**	Octacosane	0.68	0.49
85	Pentadecane	1.60	1.07	**182**	Docosane	2.46	0.79	**211**	Nonacosane	0.53	0.27
100	Hexadecane	1.61	0.52	**189**	Tricosane	2.29	0.75	**214**	Triacontane	0.27	0.39
117	Heptadecane	1.72	0.61	**196**	Tetracosane	2.46	0.94				

Table S7
BAs detected in SP_{NCHC}.

Peak	BA	RC	Peak	BA	RC	Peak	BA	RC
37	2,6-Dimethylundecane	0.16	**67**	2,6,10-Trimethyldodecane	0.26	**81**	3-Methyltetradecane	0.34

Table S8
CAs detected in SP_{NCHC}.

Peak	CA	RC	Peak	CA	RC	Peak	CA	RC	Peak	CA	RC
34	Dodec-2-ene	0.16	**99**	Hexadec-7-ene	0.27	**164**	1-Eicosene	0.25	**195**	Tetracos-9-ene	0.62
56	Tridec-2-ene	0.18	**101**	Hexadec-3-ene	0.28	**165**	Icos-3-ene	0.08	**197**	Tetracos-1-ene	0.29
69	Tetradec-2-ene	0.11	**118**	Heptadec-1-ene	0.46	**175**	10-Heneicosene	0.31	**199**	Pentacos-9-ene	0.22
72	Tetradec-5-ene	0.17	**136**	Ooctadec-9-ene	0.24	**183**	1-Docosene	0.27	**208**	Hexacos-9-ene	0.56
84	Pentadec-1-ene	0.27	**155**	Nonadec-9-ene	0.21	**188**	Tricos-9-ene	0.15			
86	Cetene	0.31	**162**	Icos-9-ene	0.27	**190**	Tricos-11-ene	0.39			

Table S9
EAs detected in SP_{NCHC} and SP_{CHC}.

Peak	EA	RC		Peak	EA	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
6	Styrene	0.07	0.01	**36**	(2-Methylbut-1-en-1-yl)benzene	0.39	0.57
10	Allylbenzene	0.05	0.06	**38**	1,3,5-Trimethyl-2-vinylbenzene	0.07	0.20
26	But-1-en-1-ylbenzene	0.15	0.46	**91**	1-Isopropenylnaphthalene	0.30	0.64
35	(3-Methylbut-2-en-1-yl)benzene	0	0.33	**179**	9-Vinylanthracene	0.12	0.33

Table S10
ABs[I] detected in SP_{NCHC} and SP_{CHC}.

Peak	AB	RC		Peak	AB	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
1	Toluene	0.18	0.10	**23**	1,2,4,5-Tetramethylbenzene	0.03	0.08
4	*m*-Xylene	0.03	0.01	**53**	1,2,3,4,5-Pentamethylbenzene	0.09	0.81
22	1,2,3,5-Tetramethylbenzene	0.01	0.06				

Table S11
TABs detected in SP_{NCHC} and SP_{CHC}.

Peak	TAB	RC in SP_{CHC}	Peak	TAB	RC in SP_{CHC}	Peak	TAB	RC	
								SP_{NCHC}	SP_{CHC}
12	1-Ethyl-2,3-dimethylbenzene	0.03	**15**	1-Ethyl-2,4-dimethylbenzene	0.03	**16**	4-Ethyl-1,2-dimethylbenzene	0.02	0.09
14	2-Ethyl-1,4-dimethylbenzene	0.02	**20**	2-Ethyl-1,3-dimethylbenzene	0.03				

Table S12
Biphenyls detected in SP_{NCHC} and SP_{CHC}.

Peak	DAB	RC		Peak	DAB	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
70	Biphenyl	0.19	0.24	**152**	3,3',4,4'-Tetramethyl-biphenyl	0.28	0.12
149	2,2',5,5'-Tetramethyl-biphenyl	0.74	0.51	**213**	5'-Phenyl-1,1':3',1''-terphenyl	1.07	2.78

Table S13
ABs[II] detected in SP_{NCHC} and SP_{CHC}.

Peak	AB	RC		Peak	AB	RC		Peak	AB	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
104	3-Methyl-biphenyl	0.40	0.67	**111**	3-Ethyl-biphenyl	0	0.20	**133**	3-Isopropyl-biphenyl	0.12	0.07
105	2-Methyl-biphenyl	1.28	0.84	**115**	4-Ethyl-biphenyl	0.09	0.16	**141**	4-Isopropyl-biphenyl	0.25	0.36
106	4-Methyl-biphenyl	0.99	1.39	**124**	2-Ethyl-biphenyl	0.14	0.16				

Table S14
DABs detected in SP_{NCHC} and SP_{CHC}.

Peak	DAB	RC		Peak	DAB	RC		Peak	DAB	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
114	2,3'-Dimethyl-biphenyl	0.31	0.71	**126**	2,4'-Dimethyl-biphenyl	0.16	0.25	**128**	4,4'-Dimethyl-biphenyl	1.71	1.89
125	3,4'-Dimethyl-biphenyl	1.47	0.71	**127**	2,2'-Dimethyl-biphenyl		0.35	**129**	3,3'-Dimethyl-biphenyl	0.15	0.15

Table S15
Anthracenes detected in SP_{NCHC} and SP_{CHC}.

Peak	Anthracene	RC		Peak	Anthracene	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
138	Anthracene	0.39	0.60	**177**	9,10-Dimethylanthracene	0.49	0.16
157	1-Methylanthracene	0.26	0.48	**180**	9-Isopropylanthracene	0.04	0.54
159	2-Methylanthracene	0.78	0.89	**184**	9-Ethyl-10-methylanthracene	0.17	0.21
166	9-Ethylanthracene	0.12	0.15				

Table S16
Phenanthrenes detected in SP_{NCHC} and SP_{CHC}.

Peak	Phenanthrene	RC		Peak	Phenanthrene	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
140	Phenanthrene	0.65	0.77	**170**	2,5-Dimethylphenanthrene	0.13	0.31
158	2-Methylphenanthrene	0.28	0.39	**171**	2,7-Dimethylphenanthrene	0.35	0.50
160	1-Methylphenanthrene	0.84	0.89	**172**	3,6-Dimethylphenanthrene	0.35	0.26
161	4-Methylphenanthrene	0.46	0.57	**173**	9,10-Dimethylphenanthrene	0.17	0.03
167	4,5-Dimethylphenanthrene	0.26	0.29	**181**	2,3,5-Trimethylphenanthrene	0.68	0.29
168	2,3-Dimethylphenanthrene	0.52	0.60	**185**	7-Isopropyl-1-methylphenanthrene	1.13	0.48
169	1,7-Dimethylphenanthrene	0.31	0.27				

Table S17
Fluorenes detected in SP_{NCHC} and SP_{CHC}.

Peak	Fluorene	RC		Peak	Fluorene	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
102	Fluorene	0.59	1.08	**143**	9,9-Dimethyl-9*H*-fluorene	0.04	0.13
121	9-Methyl-9*H*-fluorene	0.12	0.14	**145**	2,3-Dimethyl-9*H*-fluorene	0.20	0.25
122	1-Methyl-9*H*-fluorene	0.34	0.54	**146**	2-Ethyl-9*H*-fluorene	0.29	0.26
123	2-Methyl-9*H*-fluorene	0.60	1.35				

Table S18
Pyrenes detected in SP_{NCHC} and SP_{CHC}.

Peak	Pyrene	RC		Peak	Pyrene	RC		Peak	Pyrene	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
178	Pyrene	0.12	0.06	**191**	2-Methylpyrene	0.27	0.19	**194**	1,3-Dimethylpyrene	0.20	0.18
187	1-Methylpyrene	0.08	0.07	**192**	4-Methylpyrene	0.37	0.10				

Table S19
Chrysenes detected in SP_{NCHC} and SP_{CHC}.

Peak	Chrysene	RC in SP_{CHC}	Peak	Chrysene	RC in SP_{CHC}	Peak	Chrysene	RC	
								SP_{NCHC}	SP_{CHC}
204	2-Methylchrysene	0.05	**206**	1-Methylchrysene	0.14	**201**	Chrysene	0.30	0.23
205	3-Methylchrysene	0.06	**207**	6-Methylchrysene	0.17	**203**	5-Methylchrysene	0.34	0.16

Table S20
Indenes detected in SP_{NCHC} and SP_{CHC}.

Peak	Indene	RC		Peak	Indene	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
17	1-Methyl-2,3-dihydro-1*H*-indene	0.04	0.08	**49**	1,6-Dimethyl-2,3-dihydro-1*H*-indene	0	0.48
43	2-Ethyl-2,3-dihydro-1*H*-indene	0.14	0.39	**54**	5,6-Dimethyl-2,3-dihydro-1*H*-indene	0.30	0.36
45	4,7-Dimethyl-2,3-dihydro-1*H*-indene	0.22	0.51	**65**	1,1,5-Trimethyl-2,3-dihydro-1*H*-indene	0.48	0.61
46	1,3-Dimethyl-1*H*-indene	0.12		**73**	1,1,3-Trimethyl-2,3-dihydro-1*H*-indene	0.24	0.47

Table S21
Fluoranthenes detected in SP_{NCHC} and SP_{CHC}.

Peak	Fluoranthene	RC		Peak	Fluoranthene	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
176	Fluoranthene		0.10	**186**	2-Methylfluoranthene	0.41	0.10

Table S22
DHAs detected in SP_{NCHC} and SP_{CHC}.

Peak	DHA	RC		Peak	DHA	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
119	9,10-Dihydroanthracene	0.27	0.47	**144**	1-Methyl-9,10-dihydroanthracene	0.09	0.16
139	2-Methyl-9,10-dihydroanthracene	0.24	0.32				

Table S23
ADPMs detected in SP_{NCHC} and SP_{CHC}.

Peak	ADPM	RC		Peak	ADPM	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
120	Propane-1,1-diyldibenzene	0.18	0.59	**150**	Di-*m*-tolylmethane	0.08	0.19
131	1-Benzyl-4-ethylbenzene	0.05	0.22	**156**	1-Methyl-3-(4-methylbenzyl)benzene		0.12
148	Di-*o*-tolylmethane	0.13	0.20				

Table S24

Naphthalenes detected in SP_{NCHC} and SP_{CHC}.

Peak	Naphthalene	RC		Peak	Naphthalene	RC		Peak	Naphthalene	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
32	Naphthalene		1.98	**74**	2-Ethylnaphthalene	0.31	0.72	**98**	1-(*tert*-Butyl)naphthalene	0.23	0.27
58	2-Methylnaphthalene	1.23	3.04	**75**	1-Ethylnaphthalene	0.41	0.53				
63	1-Methylnaphthalene	0.72	1.64	**88**	2-Isopropylnaphthalene	0.69	1.12				

Table S25

DMNs detected in SP_{NCHC} and SP_{CHC}.

Peak	DMN	RC		Peak	DMN	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
76	1,6-Dimethylnaphthalene	0.48	2.43	**79**	2,3-Dimethylnaphthalene	0.65	1.16
77	1,3-Dimethylnaphthalene	1.50	2.79	**80**	2,6-Dimethylnaphthalene	0.78	0.58
78	2,7-Dimethylnaphthalene	1.30	1.62	**82**	1,4-Dimethylnaphthalene	0.65	0.78

Table S26

TANs detected in SP_{NCHC} and SP_{CHC}.

Peak	TAN	RC		Peak	TAN	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
93	1,4,5-Trimethylnaphthalene	0.30	0.56	**97**	2-Methyl-1-propylnaphthalene	0.83	1.12
94	1,6,7-Trimethylnaphthalene	0.56	0.90	**109**	7-Isopropyl-1-methylnaphthalene	0.27	0.29
95	2,3,6-Trimethylnaphthalene	0.49	0.63	**132**	4-Isopropyl-1,6-dimethylnaphthalene	0.06	0.15
96	1,4,6-Trimethylnaphthalene	0.43	0.73	**153**	6-Isopropyl-1,4-dimethylnaphthalene	0.15	0.20

Table S27

TMNs detected in SP_{NCHC} and SP_{CHC}.

Peak	TMN	RC		Peak	TMN	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
107	1,2,3,4-Tetramethylnaphthalene	0.18	0.28	**116**	1,4,5,8-Tetramethylnaphthalene	0.11	0.18

Table S28

OAs detected in SP_{NCHC} and SP_{CHC}.

Peak	OA	RC		Peak	OA	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
87	Acenaphthene	0.29	0.60	**200**	Triphenylene	0.34	0.34
193	5,12-Dihydrotetracene	0.32	0.13	**212**	Benzo[*a*]pyrene	0.15	0.12

Table S29
APs detected in SP_{NCHC} and SP_{CHC}.

Peak	AP	RC		Peak	AP	RC		Peak	AP	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
8	Phenol	0.30	0.34	**24**	2-Ethylphenol	0.71	1.71	**39**	2-Propylphenol	0.17	0.26
11	*o*-Cresol	0.91	1.13	**27**	4-Ethylphenol	0.73	0.90	**61**	2-Butylphenol	0.21	0.35
13	*p*-Cresol	2.28	2.82	**28**	3-Ethylphenol	1.34	1.75				

Table S30
DMPs detected in SP_{NCHC} and SP_{CHC}.

Peak	DMP	RC		Peak	DMP	RC		Peak	DMP	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
19	2,3-Dimethylphenol	0.20	0.21	**31**	3,4-Dimethylphenol	0.52	0.77	**50**	4-Ethyl-2-methylphenol	0.15	0.34
25	2,4-Dimethylphenol	2.11	2.70	**40**	4-Ethyl-3-methylphenol	0.29	0.71	**59**	3,4-Diethylphenol	0.49	0.54
29	2,5-Dimethylphenol	0.29	0.45	**42**	2-Ethyl-4-methylphenol	0.44	0.73				
30	Thymol	0.22	0.43	**44**	3-Ethyl-5-methylphenol	1.24	1.33				

Table S31
TMPs detected in SP_{NCHC} and SP_{CHC}.

Peak	TMP	RC		Peak	TMP	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
47	3,4,5-Trimethylphenol	0.19	0.22	**52**	2-Isopropyl-5-methylphenol	0.09	0.21
48	2,3,5-Trimethylphenol	0.28		**57**	2,4,5-Trimethylphenol	0.16	
51	5-Isopropyl-2-methylphenol	0.10		**60**	4-Isopropyl-3-methylphenol	0.15	

Table S32
OPs detected in SP_{NCHC} and SP_{CHC}.

Peak	OP	RC		Peak	OP	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
64	2,3,5,6-Tetramethylphenol	0.15	0.15	**142**	4-Styrylphenol	0.46	0.24
90	Naphthalen-2-ol	0.16	0.06	**154**	Anthracen-9-ylmethanol		0.02

Table S33
Esters detected in SP_{NCHC} and SP_{CHC}.

Peak	Ester	RC		Peak	Ester	RC		Peak	Ester	RC in SP_{NCHC}
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			

2	Butyl acetate	0.04	0.03	**3**	Hexyl acetate	0.04	0.05	**5**	Butyl acrylate	0.03

Table S34
Alcohols detected in SP_{NCHC} and SP_{CHC}.

Peak	Alcohol	RC		Peak	Alcohol	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
9	2-Ethylhexan-1-ol	0.18	0.07	**68**	6-Methyl-2,3-dihydro-1H-inden-4-ol	0.51	0.67
62	2,3-Dihydro-1H-inden-5-ol	0.78	1.21	**108**	9*H*-fluoren-2-ol	0.50	0.75
66	2,3-Dihydro-1H-inden-1-ol	1.49	1.38	**137**	4-Isopropylnaphthalen-2-ol	0.21	0.19

Table S35
Ketones detected in SP_{NCHC} and SP_{CHC}.

Peak	Ketone	RC		Peak	Ketone	RC		Peak	Ketone	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
7	Nonan-2-one	0.03	0.05	**89**	2-Naphthyl methyl ketone	0.13	0.22	**103**	1-(Naphthalen-1-yl)ethan-1-one	1.30	0.50

Table S36
Benzofurans detected in SP_{NCHC} and SP_{CHC}.

Peak	Benzofuran	RC		Peak	Benzofuran	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
21	2-Methylbenzofuran	0.01	0.07	**130**	1,2-Dimethylnaphtho[*2,1-b*]furan	0.11	0.20
92	Dibenzofuran	1.16	0.68	**147**	2-Methoxydibenzo[*b,d*]furan	0.08	0.13
110	4-Methyldibenzo[*b,d*]furan	1.41	1.33				

Table S37
OOCOCs detected in SP_{NCHC} and SP_{CHC}.

Peak	OOCOC	RC		Peak	OOCOC	RC		Peak	OOCOC	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
41	1-Ethyl-4-methoxybenzene	1.41	1.26	**112**	Biphenyl-4-carbaldehyde	0.12	0.22	**113**	9*H*-Xanthene	0.04	0.13

Table S38
NCOCs detected in SP_{NCHC} and SP_{CHC}.

Peak	NCOC	RC		Peak	NCOC	RC	
		SP_{NCHC}	SP_{CHC}			SP_{NCHC}	SP_{CHC}
83	*N*-Methylnaphthalen-1-amine	0.48	0.35	**134**	2-Phenazinamine	0.08	0.06

Table S39
Classification of the group components detected in SP_{NCHC} and SP_{CHC} with GC/MS.

Group component		From Table
Full name	Nomenclature	
Alkanes		
Normal alkanes	NAs	S5
Branched alkanes	BAs	S6
Alkenes		
Chain alkenes	CAs	S7
Enylarenes	EAs	S8
Arenes		
Alkylbenzenes	ABs^{I}	S9
Trialkylbenzenes	TABs	S10
Biphenyls	BPs	S11
Alkylbiphenyls	ABs^{II}	S12
Dimethylbiphenyl	DABs	S13
Anthracenes		S14
Phenanthrenes		S15
Fluorenes		S16
Pyrenes		S17
Chrysenes		S18
Indenes		S19
Fluoranthenes		S20
Dihydroanthracenes	DHAs	S21
Alkyldiphenylmethanes	ADPMs	S22
Alkylnaphthalenes	ANs	S23
Dimethylnaphthalenes	DMNs	S24
Trialkylnaphthalenes	TANs	S25
Tetramethylnaphthalenes	TMNs	S26
other arenes	OAs	S27
Oxygen-containing organic compounds	OCOCs	
Alkylphenols	APs	S28
Dimethylphenols	DMPs	S29
Trimethylphenols	TMPs	S30
Other phenols	OPs	S31
Esters		S32
Alcohols		S33
Ketones		S34
Benzofurans		S35
Other oxygen-containing aromatics	OOCAs	S36
Nitrogen-containing aromatics	NCAs	S37

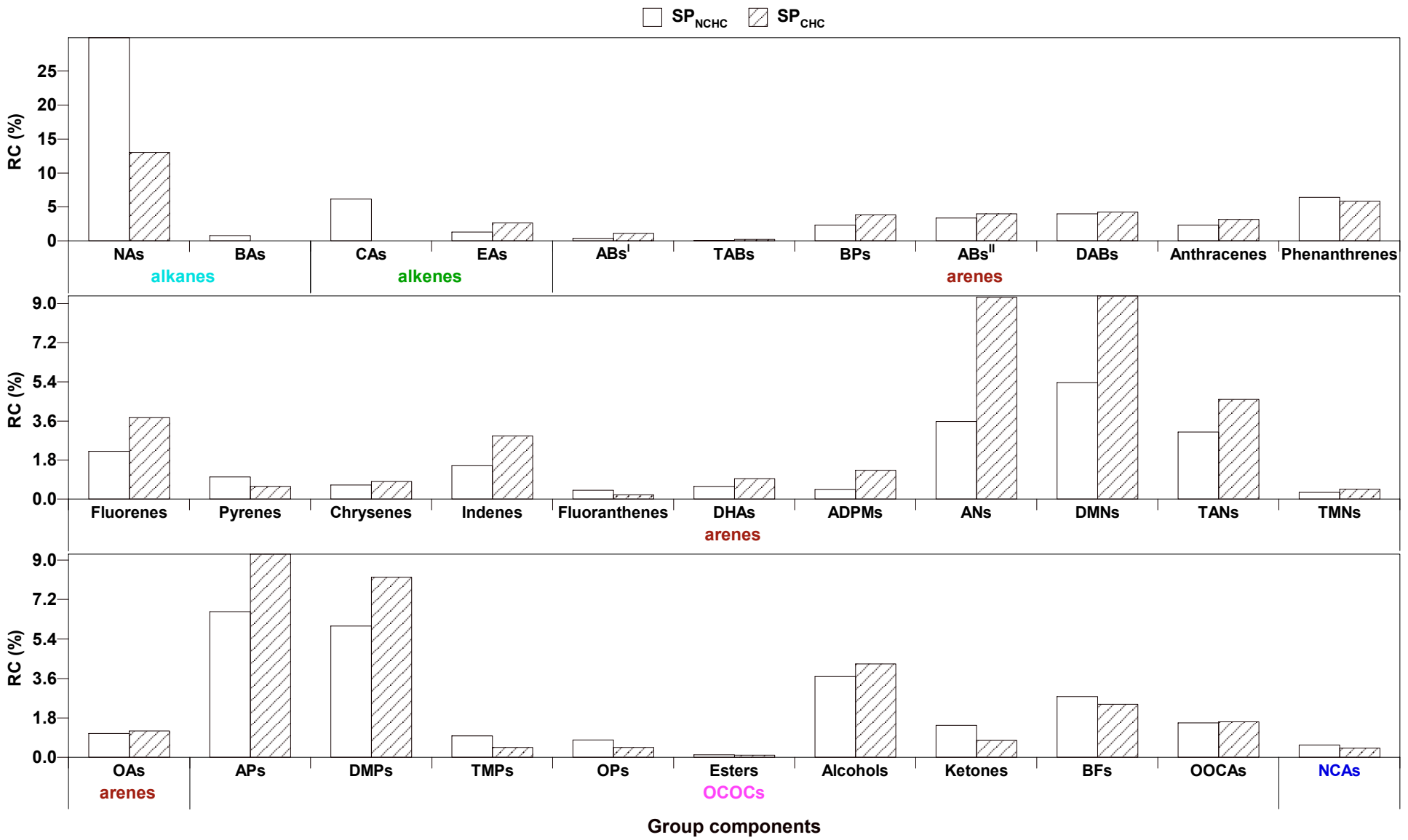

Fig. S5. The detailed distribution of group components in the SP_{NCHC} and SP_{CHC} according to the analysis with GC/MS.

Nomenclature

ARs	aromatic rings
BON	2-(benzyloxy)naphthalene
CDPs	characteristic diffraction peaks
CHC	catalytic hydroconversion
CN	carbon number
CNOFW	calcined nickel-organic framework
DBE	double bond equivalent
DCL	Direct coal liquefaction
DMF	*N*,*N*-dimethylformamide
ER	extraction residue
GC/MS	gas chromatography/mass spectrometer
ISPs	insoluble portions
IHP	initial hydrogen pressure
IMACDSMS	isometric acetone/carbon disulfide mixed solvent
NCAs	nitrogen-containing aromatics
NCHC	non-catalytic hydroconversion
NNPs	nickel nanoparticles
NOFW	nickel-organic framework
OCOCs	oxygen-containing organic compounds
QPEOTMS	quadrupole exactive orbitrap mass spectrometer
RCs	relative contents
SP_{CHC}	soluble portions from CHC
SP_{NCHC}	soluble portions from NCHC
SSBC	Shaerhu subbituminous coal
TFMSA	Trifluoromethanesulfonic acid
TG	thermogravimetric

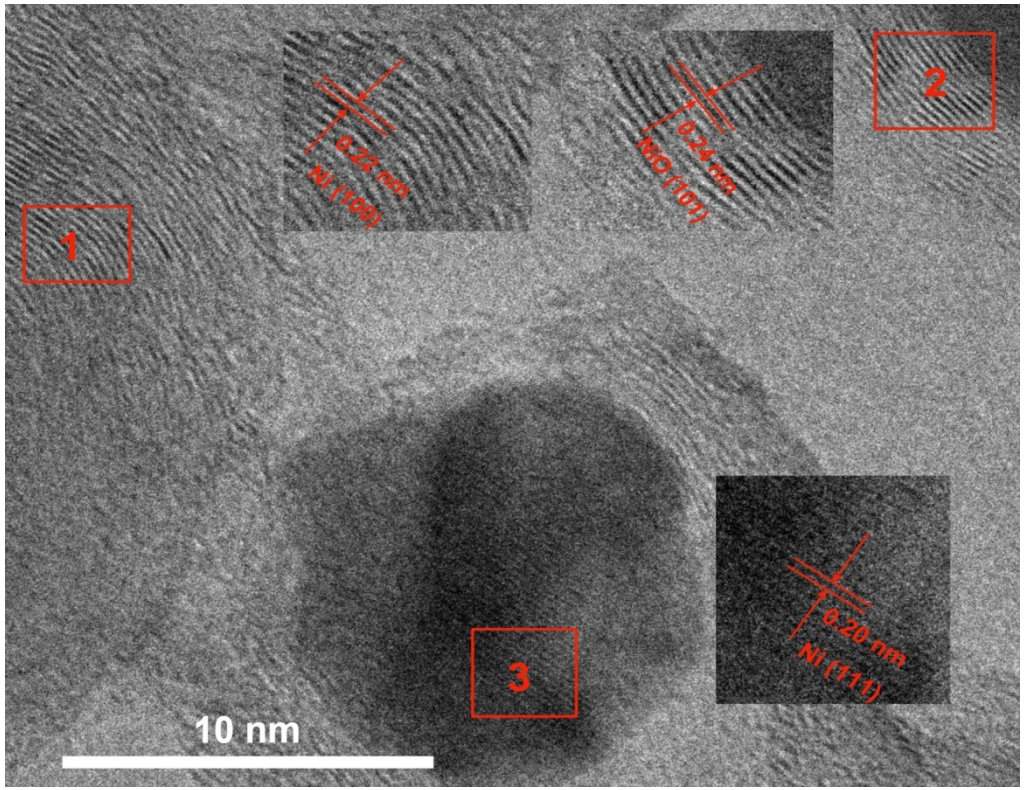

Fig. S6. TEM image of TFMSA/CNOFW.

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