catalysts

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Supplementary Materials

Acid/base-treated activated carbon catalysts for the low-temperature endothermic cracking of *n*-dodecane with applications in hypersonic vehicle heat management systems

Kyoung Ho Song [1,2], Soon Kwan Jeong [2], Ki Tae Park [2], Byung Hun Jeong [3], Kwan-Young Lee [1] and Hak Joo Kim [2,*]

1 Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seoul 02841, Republic of Korea. skh1109@kier.re.kr (K.H. Song), kylee@korea.ac.kr (K-Y. Lee)

2 Carbon Conversion Research Laboratory, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea
skh1109@kier.re.kr (K.H. Song), jeongsk@kier.re.kr (S.K. Jeong), hakjukim@kier.re.kr (H.J. Kim)

3 Agency for Defense Development, Jochiwongil 462, Yuseong-gu, Daejeon 34186, Republic of Korea
jeongbh@add.re.kr (B.H. Jeong)

* Correspondence: hakjukim@kier.re.kr ; Tel.: +82-42-860-3654 (H.J.Kim)

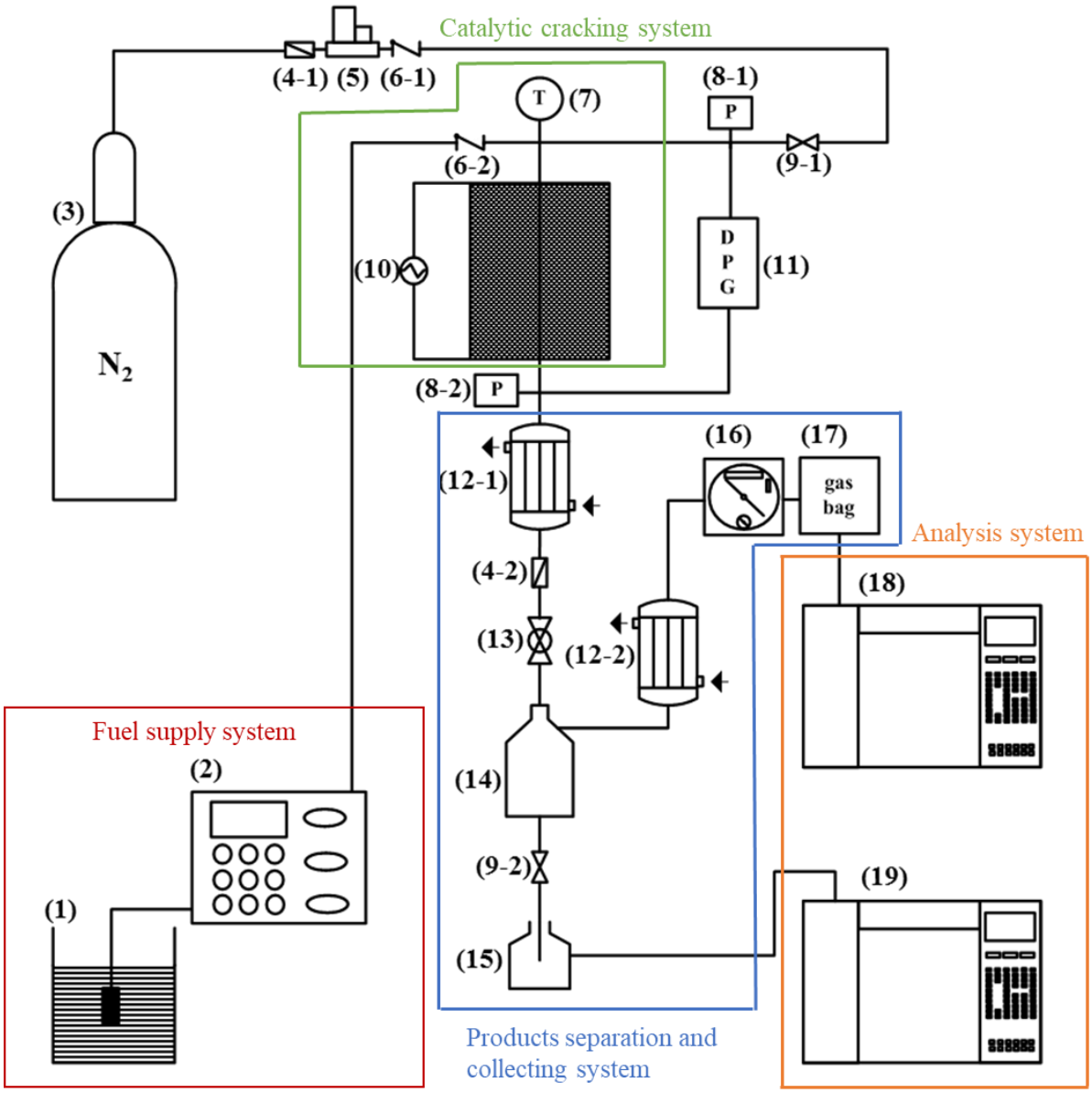

Figure S1. Experimental device for the catalytic cracking of *n*-dodecane: (1) fuel container, (2) dosing pump, (3) N_2 gas cylinder, (4) gas filter, (5) mass flow controller, (6) check valve, (7) K-type thermocouple, (8) pressure gauge, (9) on/off valve, (10) electrical heater, (11) differential pressure gauge, (12) water condenser, (13) back-pressure regulator, (14) gas-liquid separator, (15) liquid collecting vial, (16) wet gas meter, (17) gas collecting bag, (18) gas chromatograph for analysis of gaseous products, and (19) gas chromatograph for analysis of liquid products.

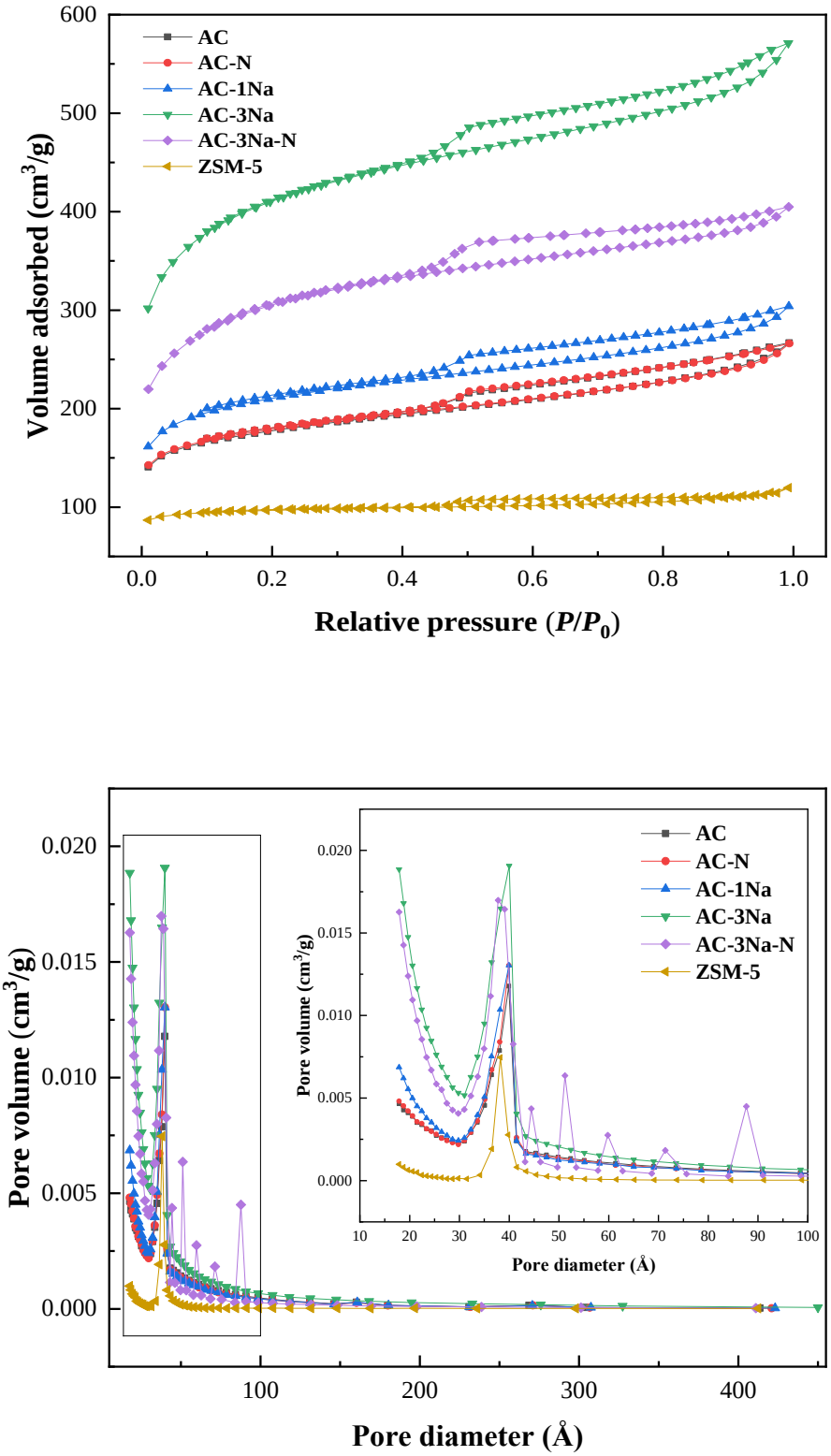

Figure S2. N_2 adsorption–desorption isotherms (a) and pore-size distributions (b) calculated using the BJH method on the fresh ACs and ZSM-5 zeolite.

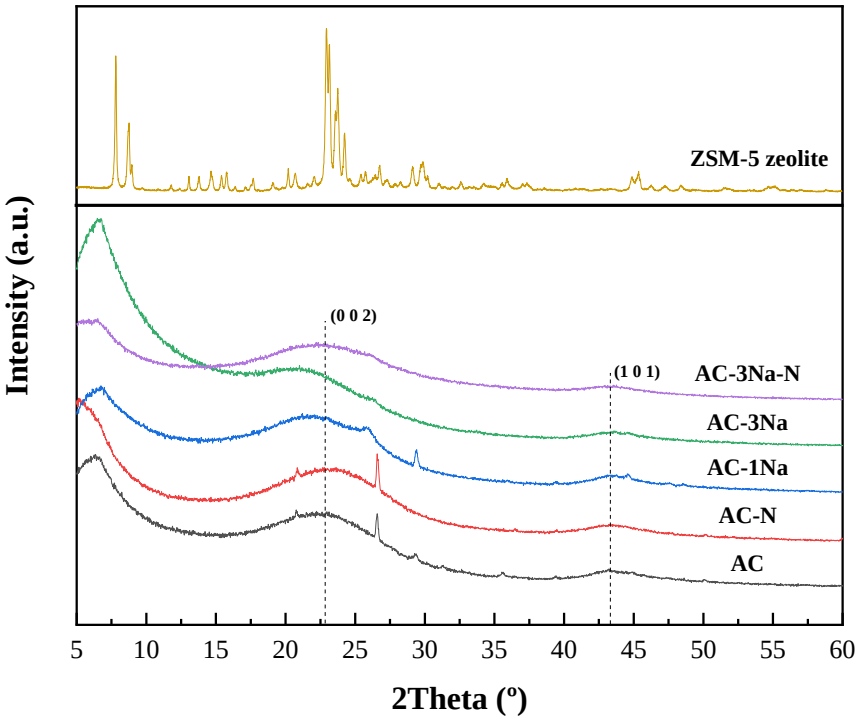

Figure S3. XRD patterns of the fresh ACs and ZSM-5 zeolite.

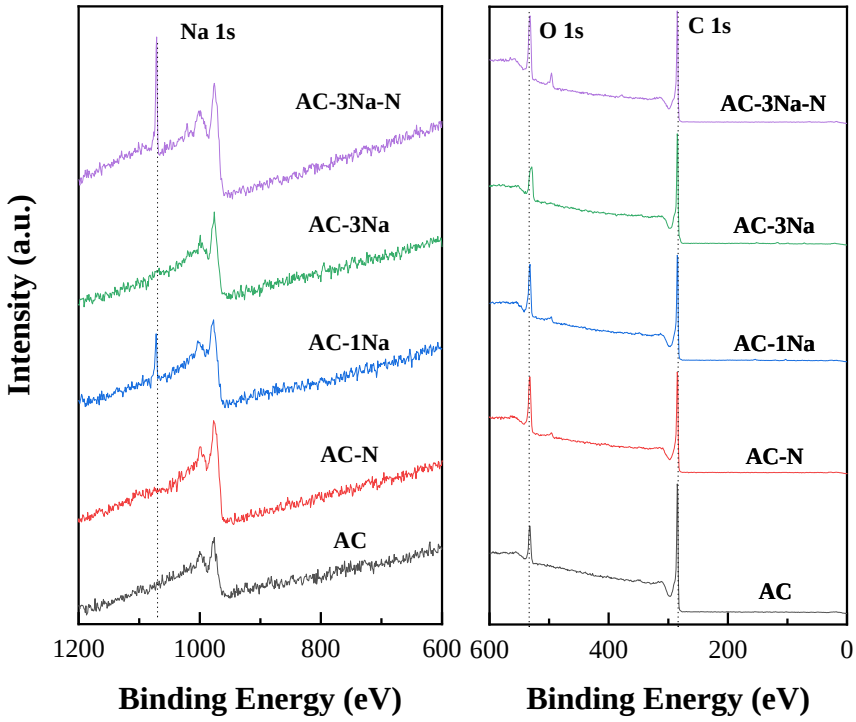

Figure S4. X-ray photoelectron spectroscopy survey scans of AC catalysts (B.E. = binding energy).

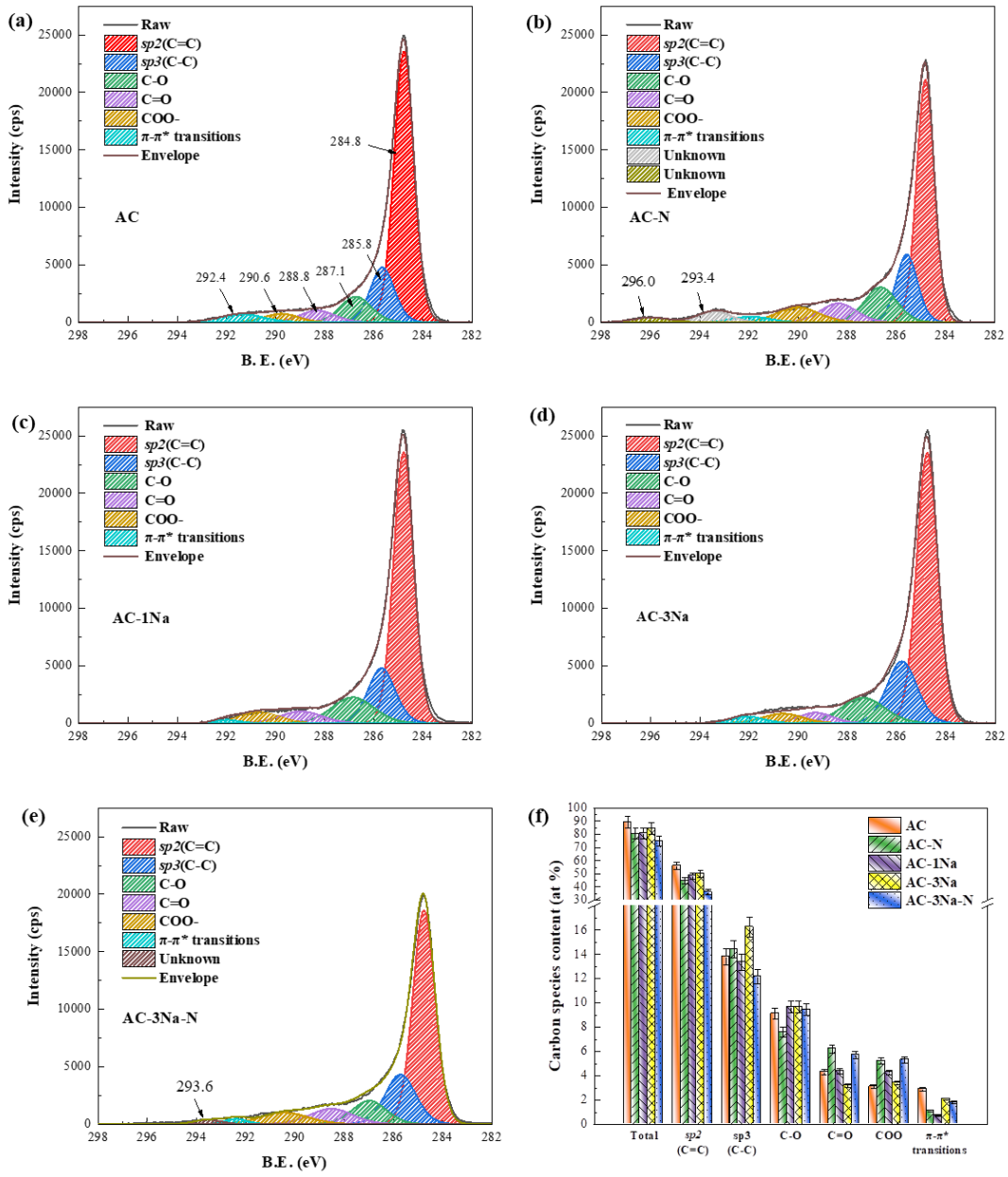

Figure S5. Deconvolution of the XPS C1s spectra of the AC catalysts: (a) AC, (b) AC-N, (c) AC-1Na, (d) AC-3Na, (e) AC-3Na-N, and (f) carbon species content (B.E. = binding energy).

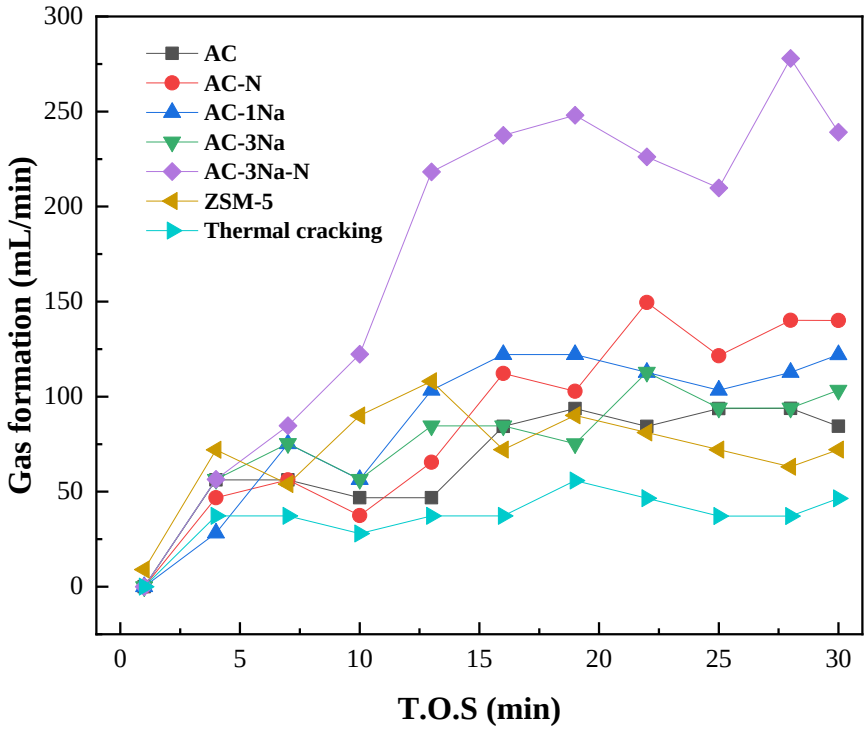

Figure S6. Gas formation profiles over ACs and ZSM-5 at 450 °C and 4 MPa.

Table S1 Energy-dispersive X-ray analysis (EDX) and surface concentration (at%) determined by XPS of the ACs.

Sample	EDX (at%)				XPS (at %)			
	C	O	N	Na	C 1s	O 1s	N 1s	Na 1s
AC	90.2	9.8	·	·	89.1	10.5	0.4	·
AC-N	85.2	14.8	·	·	80.5	18.4	1.1	·
AC-1Na	83.9	14.0	·	2.1	80.8	17.5	0.8	0.9
AC-3Na	91.1	8.6	·	0.3	84.4	15	0.2	0.4
AC-3Na-N	76.1	22.5	·	1.4	75.2	21.8	0.7	2.4

Table S2 Lattice spacings (d002) and crystallite sizes (τ) of the ACs.

Catalyst	d_{002} (nm)	Lc (nm)
AC	0.3868	11.08
AC-N	0.3787	10.53
1AC	0.3965	11.79
3AC	0.4050	12.97
3AC-N	0.3865	9.70

Table S3 Assignments of FT-IR vibration bands in Fig. 5.

No.	Peak (cm^{-1})		Surface group	Assignment	Reference
	This work	Reference			
1	1128	1118	COH	Phenolic group, OH stretch	[56]
2	1571	1558	C=O	Ketone, C=O stretch	[54],[55]
3	1710	1698	COO	Carboxylic acid, COO stretch	[54]
	2916, 2844	2920, 2850	CH_2	Asymmetric and symmetric CH_2 stretch	[53]
5	3663~3002	3200~3600, 3100~3600	O-H	O-H stretch	[49],[50]

Table S4 Effects of AC and ZSM-5on the liquid products of n-dodecane cracking as determined by GC-DHA.

Component	Thermal cracking	AC	AC-N	AC-1Na	AC-3Na	AC-3Na-N	ZSM-5
propane	0.3418		0.2857	0.185	0.1985	0.1497	
isobutane							0.1566
isobutylene	0.6972	0.0962	1.1331	1.0308	1.0119	0.7649	0.4144
n-butane	0.6787	0.1329	1.0433	1.0268	1.0486	0.6833	0.7814
trans-2-butene	0.0677		0.261	0.243	0.2071	0.274	0.1354
cis-2-butene	0.0527		0.2195	0.2054	0.174	0.2432	0.1145
2,2-dimethylpropane			0.0434	0.0435		0.0497	
isopentane			0.1123	0.1138	0.0922	0.132	0.5621
1,2-butadiene				0.3688		0.0482	
1,4-pentadiene	0.3019				0.1032	0.1857	0.129
1-pentene	1.2412	0.8767	2.5859	2.1739	2.4655	2.1086	1.0288
2-methyl-1-butene			0.0979	0.1002	0.0801	0.1142	0.2753
n-pentane	0.9598	0.7608	1.8253	2.0232	1.9392	1.484	1.647
trans-2-pentene	0.0857	0.1338	0.4017	0.4319	0.3563	0.4838	0.3054
cis-2-pentene	0.046	0.0747	0.2232	0.2395	0.1967	0.2752	0.1745
2-methyl-2-butene			0.0759	0.0752	0.0544	0.1289	0.6149
trans-1,3-pentadiene		0.0482	0.1439	0.1539	0.1198	0.2099	0.047
cyclopentadiene		0.0538	0.1661	0.1781	0.1295	0.301	0.0508
cyclopentene			0.2392	0.2403	0.1692	0.4018	0.0524
4-methyl-1-pentene			0.0751	0.0779	0.0557	0.106	0.0434
3-methyl-1-pentene			0.0632	0.0681	0.053	0.0803	0.0478
cyclopentane				0.1661	0.1153	0.2895	0.0561
2,3-dimethylbutane		0.0675	0.196				0.0576
4-methyl-*trans*-2-pentene							0.0749
2-methylpentane			0.0668	0.0715	0.0565	0.0797	0.3814
3-methylpentane			0.0508	0.0546	0.0437	0.061	0.1731
2-methyl-1-pentene							0.123
1-hexene	2.0538	2.5688	4.7277	4.0589	4.0208	3.8521	2.1621
n-hexane	0.8599	1.1017	1.6061	1.3588	1.7615	1.4374	1.442
diisopropylether							0.0719
2-ethylbutene-1		0.0337					
cis-3-hexene			0.0597	0.0707	0.0617	0.0745	0.2249
trans-3-hexene	0.0938						
trans-2-hexene			0.5679	0.4096	0.3398	0.4288	0.2204
2-methyl-2-pentene		0.0603	0.0361	0.0385		0.0476	0.0492
3-methyl-*cis*-2-pentene			0.1274	0.1338	0.0964	0.1917	
3-methylcyclopentene		0.0312	0.0695	0.072	0.0497	0.1162	0.1106
cis-2-hexene	0.0492	0.1129	0.1924	0.2178	0.1813	0.2313	
3,3-dimethyl-1-pentene			0.0409	0.0466	0.0384	0.0575	
methylcyclopentane	0.0697	0.1894	0.5631	0.3745	0.2748	0.5005	0.2209
2,4-dimethylpentane							0.0906
2,3,3-trimethyl-1-butene						0.0344	0.0392
4,4-dimethyl-*cis*-2-pentene							0.1498
1-methylcyclopentene	0.0305	0.1685	0.1915	0.2006	0.1461	0.2823	0.1098
3-methyl-1-hexene			0.5857	0.3312	0.3248	2.3562	
5-methyl-1-hexene							0.0594

3,3-dimethylpentane			0.1132	0.1189	0.0873	0.1507	
2-methyl-*trans*-3-hexene							0.0547
diolefin		0.174	0.1642	0.1763	0.1298	0.2628	0.0454
4-methyl-*trans*/*cis*-2-hexene				0.0345		0.0362	0.0552
2-methylhexane						0.0359	0.1667
1,1-dimethylcyclopentane			0.3499	0.36	0.248	0.5977	
3-methylhexane							0.1382
cyclohexene	0.0328		0.0422	0.0469	0.0376	0.0461	0.075
3,4-dimethyl-*cis*-2-pentene							0.0529
4-methylhexene-1		0.0526					
5-methylhexene-1		0.0618					
t-amylmethylether		0.2384					
3-methylhexane		0.0361					
5-methyl-*cis*-2-hexene				0.0458			
cis-1,3-dimethylcyclopentane							0.0467
trans-1,3-dimethylcyclopentane			0.0369	0.0398		0.0515	0.07
trans-1,2-dimethylcyclopentane				0.1055			
3-ethylpentane			0.1544		0.0892	0.1246	0.0685
1-heptene	1.7974	0.0697	3.8067	3.1833	3.1612	3.1173	1.9575
trans-3-heptene		0.0803	0.1261	0.1408	0.1195	0.1564	0.9284
n-heptane	0.7417	1.1033	1.2886	1.2966	1.0284	1.19	0.1432
3-methyl-*trans*-3-hexene							0.1177
cis-3-heptene			0.2144	0.2415	0.2101	0.227	0.042
trans-2-heptene	0.0702	0.1653					
3-methyl-*trans*-2-hexene						0.0567	0.1091
2,3-dimethyl-2-pentene	0.0381		0.1186	0.1372	0.1131	0.1289	0.0958
3-ethylcyclopentene			0.0419	0.0452	0.0314	0.0621	
cis-1,2-dimethylcyclopentane		0.0468	0.0503	0.0805	0.0594	0.0569	0.1088
methylcyclohexane	0.0712	0.1701	0.2527	0.2736	0.2074	0.2885	
O36			0.1151	0.1229	0.0933	0.1517	
ethylcyclopentane		0.0728					
2,4-dimethylhexane							0.0501
2,2,3-trimethylpentane			0.1313	0.1406	0.103	0.1958	0.0623
2,5-dimethylhexane		0.1373	0.2223	0.2324	0.1591	0.3543	
1t,2c,3-trimethylcyclopentane						0.0518	0.0946
O40						0.0514	
toluene		0.1881					
O42						0.0647	
O44							0.0703
O45		0.0725	0.1659	0.1033	0.0776	0.1573	
1-octene	1.609	2.4583	2.7312	2.3391	2.015	2.5497	1.7095
trans-3-octene				0.0942	0.0816		
n-octane	0.6425	1.0344	1.0794	1.0614	1.2152	0.9711	0.6912
trans-2-octene			0.1306	0.1481	0.1331	0.124	0.078

3,3-dimethylheptene-1		0.1195					
O50							0.0796
cis-2-octene				0.0798	0.0729		
1,1,4-trimethylcyclohexane						0.1026	
3,5-dimethylheptane						0.1151	
N8			0.1299	0.1135		0.4406	
ethylbenzene							0.0835
2-methyl-2-octene						0.3676	
1,3-dimethylbenzene							0.3224
N12						0.1906	
1,4-dimethylbenzene							0.2553
1,2-dimethylbenzene							0.1267
1-nonene	1.4389	2.2148	2.9009	2.065	2.2011	2.1301	1.5432
n-nonane	0.7034	1.0619	1.005	1.1529	1.1431	0.8749	0.6449
trans-nonene		0.0865	0.0859	0.098	0.0876	0.079	
i-propylbenzene		0.0442					
n-propylbenzene		0.0542					
cis-2-nonene			0	0	0	0	
2,5-dimethyloctane						0.0742	
1,3-methylethylbenzene						0.0593	0.2025
1,4-methylethylbenzene							0.133
5-methylnonane				0.0539		0.0898	
I18						0.067	
1,2,4-trimethylbenzene							0.1981
1-decene	1.5108	2.2598	2.7671	2.3036	2.1045	2.0453	1.5715
n-decane	0.1772	0.3502	0.3078	0.3999	0.4213	0.252	0.1549
1,2,3-trimethylbenzene			0.0428	0.0503	0.0413	0.0435	
I28						0.092	
1,3-diethylbenzene							0.0484
I33			0.0983	0.066	0.0513	0.0912	0.0802
1,4-methyl-n-propylbenzene		0.049					
1-undecene	0.5079	0.8259	0.8293	0.8527	0.7909	0.7778	0.5578
n-undecane	0.4696	0.506	0.4292	0.4477	0.4724	0.3759	0.4088
1,2-methyl-*n*-butylbenzene						0.029	
2-methylindan						0.0589	
1,3-methyl-*n*-butylbenzene						0.0308	
I47			0.1186	0.1692	0.2185	0.0947	
1-dodecene	0.1149	0.3415	0.3192	0.2692	0.3044	0.2498	0.1307
I48			0.0675	0.0679	0.0852	0.037	
1,3-dipropylbenzene		0.0457	0.0794	0.1083	0.1396	0.0609	
n-dodecane	81.9198	75.3684	58.9978	61.8205	64.7501	55.4715	72.3249
1-tridecene		0.0292				0.1531	0.0349
n-tridecane	0.0868	0.0893	0.0736	0.0745	0.0754	0.0638	0.0654
Total oxygenates	0	0.238	0	0	0	0	0.072
Total heavies	0.035		0.036	0.034	0.034	0.108	0
Total unknowns	0.403	3.643	2.27	2.618	1.669	5.848	1.504
Grand total	100	100	100	100	100	100	100

Table S5 Catalytic performance of supercritical catalytic cracking of *n*-dodecane in the references.

Sample	Reactant	Catalyst packed type	Reaction pressure /MPa	Reaction Temp. /°C	Flow rate	Conv. /%	Gas yield /%	Heat sink /kJ·kg^{-1}	Reference
NC	*n*-dodecane	Wall-coated	4	550	10 mL·min^{-1}	41.01	53.12	·	[1]
HZ-TPO	*n*-dodecane	Wall-coated	4	500	10 mL·min^{-1}	55.07	60.18	·	[2]
HZ-C16&T	*n*-dodecane	Wall-coated	4	500	10 mL·min^{-1}	57.97	55.09	·	[2]
ZTA	*n*-decane	Wall-coated	2.5	750	1 g/s	84.1	·	3540	[3]
Mo-ZTA	*n*-decane	Wall-coated	2.5	750	1 g/s	88.4	·	3790	[3]
MFI-Al	*n*-dodecane	Wall-coated	4	550	5 mL·min^{-1}	·	57.85	2865	[4]
MFI-Ga	*n*-dodecane	Wall-coated	4	550	5 mL·min^{-1}	·	67.30	3040	[4]
ZSM-5-0.5P	*n*-dodecane	Wall-coated	4	550	5 mL·min^{-1}	·	64.21	3094	[5]
ZSM-5-Na	*n*-dodecane	Wall-coated	4	550	5 mL·min^{-1}	63.25	·	2826	[6]
1.0 Ag-NZC	*n*-dodecane	Wall-coated	4	550	5 mL·min^{-1}	37.51	·	·	[7]
HZC-ER	*n*-dodecane	Wall-coated	4	500	10 mL·min^{-1}	53.32	·	·	[8]
HZC-MR	*n*-dodecane	Wall-coated	4	550	5 mL·min^{-1}	37.51	·	·	[8]
ZSM-5	*n*-dodecane	Fixed	4	450	1 mL·min^{-1}	48.3	24.3	2502	[9]
AC-673	*n*-dodecane	Fixed	4	450	1 mL·min^{-1}	72.3	48.3	2716	[9]
AC-3Na-N	*n*-dodecane	Fixed	4	450	1 mL·min^{-1}	77.4	61.1	3223.6	This work

Table S6 GC conditions for liquid product analysis.

Liquid analysis (Agilent 7890 B GC)			
Oven	Rate (℃/min)	Value (℃)	Hold Time (min)
		30	15
	5	45	65
	1.6	200	5.12
	10	250	10
Inlet	Heater (℃)	250	
	Pressure (kPa)	306	
	Total flowrate (mL/min)	223.38	
	Inlet-mode	Split mode	
	Split ratio	100:1	
Column DB-5 capillary (AC 25190.300)	Length (m)	100	
	Diameter (μm)	250	
	Film thickness (μm)	0.5	
	Flow rate (ml/min)	2.172	
	Holdup time (min)	6.202	
	Pressure(kPa)	306	
Injection (Agilent 7693 A autosampler)	Syringe size (μl)	10	
	Injection volume (μl)	0.1	
Detector	Type	Flame Ionization Detector (FID)	
	Heater (℃)	250	
	H_2 flowrate (ml/min)	35	
	Air flowrate (ml/min)	350	
	Makeup flow (ml/min)	20 (He)	

Table S7 GC conditions for gaseous product analysis.

Gas analysis (Younglin, 6500YL)			
Oven	Rate (℃/min)	Value (℃)	Hold Time (min)
		50	3
	20	120	7
	20	220	5
Inlet	Heater (℃)	250	
	Pressure (kPa)	278.1	
	Total flowrate (mL/min)	203	
	Inlet-mode	Split mode	
	Split ratio	200:1	
Column GS-GasPro capillary	Length (m)	30	
	Diameter (mm)	0.32	
	Film thickness (μm)	0.5	
Injection (Manual injection)	Syringe size (μl)	500	
	Injection volume (μl)	500	
Detector	Type	Flame Ionization Detector (FID)	
	Heater (℃)	300	
	H_2 flowrate (ml/min)	40	
	Air flowrate (ml/min)	300	
	Makeup flow (ml/min)	20 (Ar)	

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