Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Catalytic degradation of pine sawdust over heterotopic Ca-Fe and HZSM-5 to produce aromatic hydrocarbons

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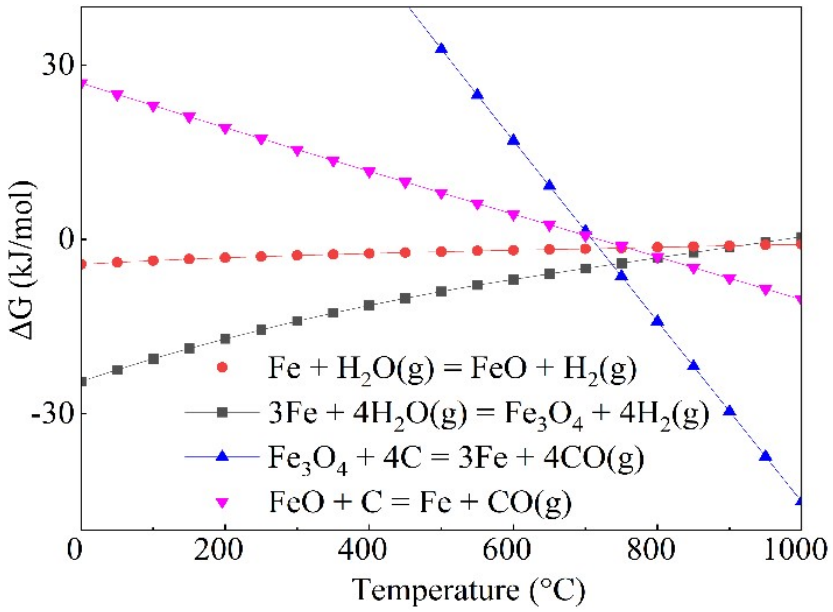

Fig. S1 Gibbs free energies for the reactions of iron catalyst with water and carbon at different temperatures.

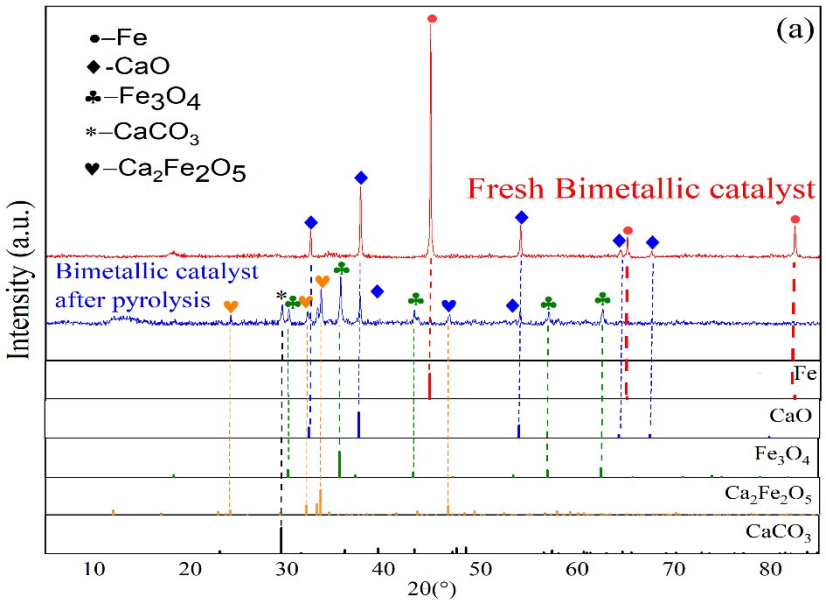

Fig. S2 XRD patterns of bimetallic catalysts before and after pyrolysis.

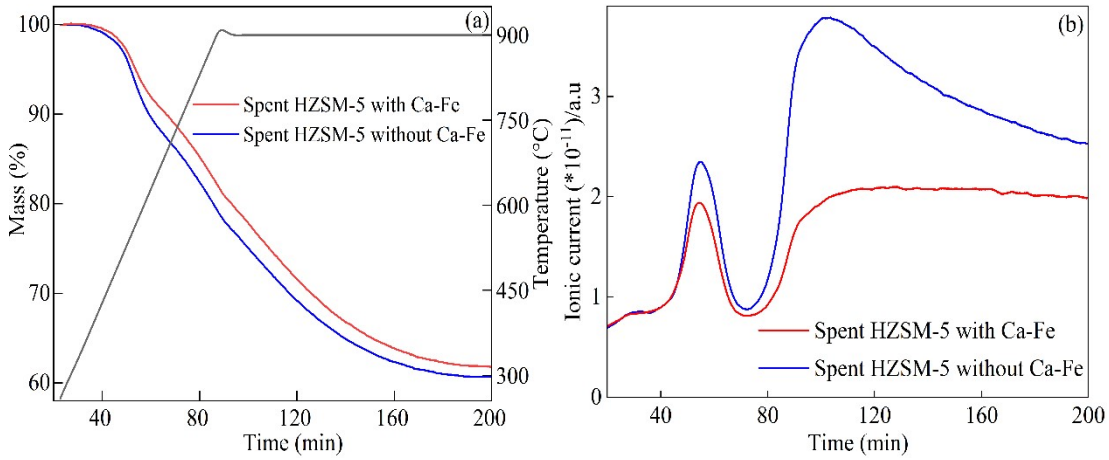

Fig. S3 (a) TG curves and (b) ionic current intensity of CO_2 for HZSM-5 after pyrolysis.

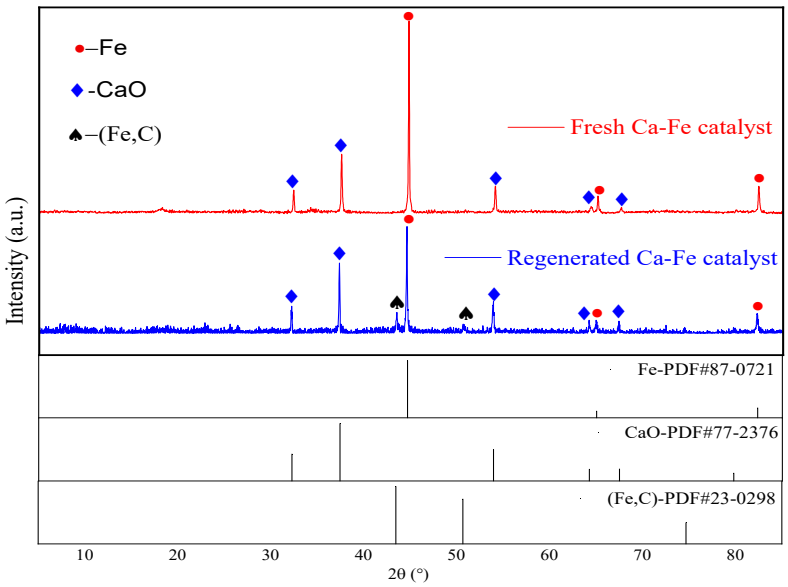

Fig. S4 XRD patterns of fresh Ca-Fe catalyst and regenerated Ca-Fe catalyst.

Table S1 The detailed reaction conditions

No.	Ca-Fe to HZSM-5 ratio	Temperature (°C)	Catalysts to pine sawdust ratio
1	0:1	600	2:1
2	1:2	600	2:1
3	1:1	600	2:1
4	2:1	600	2:1
5	1:0	600	2:1

6	1:1	450	2:1
7	1:1	500	2:1
8	1:1	550	2:1
9	1:1	600	2:1
10	1:1	650	2:1
11	1:1	600	0:1
12	1:1	600	1:1
13	1:1	600	2:1
14	1:1	600	3:1

Table S2 Calibration equations and correlation coefficients for the aromatic products

Aromatics	Calibration equations	Correlation coefficients, R^2
benzene	y = 614242.6482x - 219673.7989	0.997
toluene	y = 953897.9604x - 405341.7278	0.998
ethylbenzene	y = 1092883.5058x + 82135.1803	0.999
m-xylene	y = 2279600.7678x - 166073.3567	0.999
o-xylene	y = 1248772.704x + 1337487.0079	0.999

Table S3 Concentration of gaseous products in the overall reactor effluent from catalytic pyrolysis of pine sawdust (%)

Reaction conditions		H_2	CO_2	CH_4	CO
Ca-Fe/ HZSM-5 mass ratio	0:00	0.7484	1.1777	0.1838	1.2265
	1:00	2.2000	0.1922	0.2061	1.0900
	1:02	1.8899	0.7921	0.2438	1.4327

	1:01	2.3567	0.2815	0.2358	1.4029
	2:01	2.8199	0.1391	0.1971	1.2645
	0:01	0.8434	1.3143	0.2050	1.3922
Temperature	450	0.9391	1.3069	0.1110	0.8178
	500	1.4427	1.0462	0.1532	1.0675
	550	2.0170	0.6324	0.2001	1.4087
	600	2.3567	0.2815	0.2358	1.4029
	650	2.0859	0.4857	0.2388	1.5210
Catalysts/pine sawdust ratio	0:01	0.7484	1.1777	0.1838	1.2265
	1:01	1.8391	0.6780	0.2290	1.4281
	2:01	2.3567	0.2815	0.2358	1.4029
	3:01	2.6533	0.0835	0.2348	1.3547

Table S4 Compositions of bio-oil from pine sawdust pyrolysis at different conditions (peak area percentage/%).

Compound	Ca-Fe to HZSM-5 ratio					Temperature				Catalysts to biomass ratio		
	1:0	1:2	1:1	2:1	0:1	450	500	550	650	0:1	1:1	3:1
Mono-aromatic hydrocarbons (MAHs)												
Benzene	3.06	7.99	9.37	8.50	7.61	5.98	6.31	8.02	12.66	0.78	12.97	11.97
Toluene	3.06	20.02	21.45	18.32	16.79	13.86	15.69	18.77	23.19	0.91	15.83	23.81
Ethylbenzene	0.27	1.50	1.74	1.31	1.15	1.30	1.30	1.20	0.85	0	1.32	1.02
Benzene, 1,3-dimethyl-	0.75	10.77	10.65	10.19	9.04	7.92	8.97	10.11	7.18	0.20	4.85	8.94
Styrene	0.38	0	0.54	1.43	0.43	0	0.72	0.28	0.66	0	0.46	0.62
O-xylene	0.29	2.26	2.08	2.01	1.66	1.18	1.21	1.63	1.46	0	1.29	2.10
Benzene, 1-ethyl-4-methyl-	0	0	1.04	0.95	0.49	1.46	1.27	1.27	0.74	0	1.36	0.79
Mesitylene	0	0.31	1.54	0.76	0.29	1.61	1.34	1.42	0.62	0	0.94	0.65
Benzene, 1-propynyl-	0	0	1.14	0.94	0.33	0	0.56	0.69	0.82	0	0.36	1.04
Benzene, 1,3,5-trimethyl-2-(1,2-propadienyl)-	0	0.27	1.38	1.16	0.28	0	0.96	0.39	0.34	0	0.64	0.62
Poly-aromatic hydrocarbons (PAHs)												
Indane	0	1.65	1.34	0.73	0	1.44	1.51	1.36	1.48	0	0.96	1.54

Naphthalene, 1,2-dihydro-	0	2.85	2.49	2.51	2.97	3.15	3.1	2.47	2.62	0	2.24	2.65
Naphthalene	0	2.38	1.98	0.83	2.84	2.66	2.65	2.2	2.4	0	1.5	2.24
Naphthalene, 2-methyl-	0	4.63	4.89	5.03	4.83	5.49	5.67	5.02	4.93	0	2.84	5.02
Naphthalene, 2-ethyl-	0	1.62	1.82	0.93	1.77	2.02	1.88	1.88	1.92	0	1.68	1.82
Naphthalene, 2,6-dimethyl-	0	3.77	4.23	3.74	3.81	4.66	4.55	4.31	4.63	0	3.34	4.43
Naphthalene, 2-ethenyl-	0	1.55	1.26	1.62	1.57	1.48	1.42	1.38	1.64	0	0.92	1.48
1-Naphthalenol, 5,8-dihydro-	0	1.46	1.19	1.12	1.65	1.41	1.08	1.16	1.25	0	0.68	1.32
Naphthalene, 1-propyl-	0	1.23	0.92	1.25	1.28	0	0.98	0.90	0.93	0	0	1.05
Naphthalene, 1,6,7-trimethyl-	0	1.63	1.64	1.24	1.65	1.87	1.77	1.68	1.88	0	0.98	1.66
Fluorene	0	1.43	1.57	1.62	1.43	1.42	1.02	0.94	1.95	0	1.5	1.68
Naphthalene, 2-methyl-1-propyl-	0	0.98	0.94	1.34	1.87	1.34	1.28	1.22	1.58	0	0.68	1.06
9H-Fluorene, 9-methyl-	0	1.76	1.32	1.69	1.65	1.64	1.36	1.38	1.38	0	1.45	1.52
Phenanthrene	0	1.21	1.46	1.94	1.45	1.68	1.53	1.50	1.06	0	1.02	1.82
Anthracene	0	3.24	3.31	3.93	3.82	3.52	3.42	3.36	3.62	0	3.28	3.52
9H-Fluorene, 9,9-dimethyl-	0	1.42	0.92	0	1.35	0	0	0.88	0.98	0	1.06	1.25
Anthracene, 2-methyl-	0	0.97	1.27	1.28	1.26	1.76	1.54	1.31	1.28	0	1.36	1.09
Phenanthrene, 2-methyl-	0	2.48	2.63	2.53	2.61	2.84	2.8	2.82	2.31	0	2.08	2.78
Phenanthrene, 1,7-dimethyl-	0	1.66	1.63	1.82	1.89	1.74	1.68	1.66	1.68	0	1.66	2.06
Phenanthrene, 2,3-dimethyl-	0	1.22	0.94	1.26	1.26	0	0	0.69	0.92	0	0.84	1.05
Anthracene, 1,4-dimethyl-	0	1.44	1.78	1.51	1.68	2.00	2.02	1.94	1.82	0	1.69	1.92
Methoxyphenols (MPHs)												
Phenol, 2-methoxy-	1.42	0.51	0.50	0.57	0.64	0.94	0.78	0.67	0.53	4.22	0.86	0.24
2-Methoxy-5-methylphenol	3.20	1.54	0.80	1.29	1.86	3.30	2.92	1.92	0.77	9.24	2.24	0.32
Phenol, 4-ethyl-2-methoxy-	1.04	0.74	0.32	0.88	0.83	0.38	0.38	0.35	0	2.44	0.70	0
Phenol, 2,6-dimethoxy-	0.92	0.13	0	0.42	0.54	0.66	0.52	0	0	3.03	0.64	0
Phenol, 2-methoxy-4-propyl-	2.06	1.19	0.39	0.82	1.27	2.14	2.24	1.88	0.64	7.42	1.62	0.12
Phenols (PHs)												
Phenol	9.45	2.36	0.66	1.59	1.25	0.10	0.62	0.62	0.86	1.56	0.94	0.62
Phenol, 2-methyl-	7.06	0.92	0.42	0.76	1.59	0	0	0.15	0.22	4.56	2.32	0.54
p-Cresol	6.36	1.17	0.29	1.02	0.93	0	0.26	0.29	0.32	3.11	1.68	0.22
Phenol, 2,4-dimethyl-	1.84	0	0	0	0	0	0	0	0	0.64	0.43	0
Catechol	1.28	0.27	0.32	0.82	0.84	0.12	0.24	0.28	0.32	2.36	1.02	0.20
Phenol, 3,4-dimethyl-	0.25	0	0	0	0	0	0	0	0	0	0	0
Phenol, 3-ethyl-	1.26	0	0	0	0	0	0	0	0	0	0	0
1,2-Benzenediol, 3-methyl-	5.20	0.82	0.25	0.65	1.21	0.13	0.22	0.24	0.64	4.04	2.81	0.34
1,3-Benzenediol, 4,5-dimethyl-	3.26	0.30	0	0.13	1.62	0.14	0.28	0.22	0	2.24	1.46	0
Other oxygenates (Acids, Ketones, Furans, Anhydrosugars)												
Acetic acid	0	0	0	0	0.26	0.82	0.38	0	0	8.86	0	0
Homovanillic acid	0	0	0	0	0	0.28	0	0	0	2.42	0	
2-Propanone, 1-hydroxy-	5.36	0.48	0.39	0.55	0.29	0.84	0.84	0.42	0.28	4.62	1.34	0
1-Hydroxy-2-butanone	5.33	0	0	0	0	1.13	0.46	0	0	4.67	0.54	0
2(5H)-Furanone	1.96	0	0	0	0.44	0.21	0	0	0	0	0.56	0
1,2-Cyclopentanedione	8.28	1.32	1.18	1.17	0.61	3.42	2.72	2.44	1.09	6.96	1.62	0.53
2-Cyclopenten-1-one, 3-methyl-	0.96	0	0	0	0.66	0.82	0.42	0	0	0	0	0
3-Penten-2-one	4.82	0.54	0.62	0.76	0.27	0.40	0.28	0.28	0.64	4.37	1.02	0
Ethanone, 1-(2-hydroxy-5-	9.64	1.56	0.45	1.80	1.07	3.24	2.73	2.62	0.48	9.37	3.28	0.34

methylphenyl)-												
.beta.-D-Glucopyranose, 1,6-anhydro-	0	0	0	0	0	0.62	0	0	0	2.74	0	0
Furfural	0.59	0.24	0.38	0.24	0.62	0.32	0.24	0.42	0.40	0.98	0.52	0.28
Benzofuran, 2,3-dihydro-	5.26	0.38	0.41	0.65	0.36	2.55	1.98	1.52	0.45	3.52	0.51	0.33
Benzofuran, 2-methyl-	1.79	0.16	0.62	0.44	0.64	0.62	0.72	0.58	0.55	1.62	0.60	0.36
Benzofuran, 2,3-dihydro-2-methyl-7-phenyl-	1.62	0	0	0	0.42	0	0	0	0	1.35	0	0

Table S5 Specific surface area and pore volume of HZSM-5

Catalysts	S_{BET} ($m^2 \bullet g^{-1}$)	V ($cm^3 \bullet g^{-1}$)
Fresh HZSM-5	519.773	0.3598
Spent HZSM-5 without Ca-Fe	318.053	0.2244
Spent HZSM-5 with Ca-Fe	397.574	0.2625