Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Effects of controllable mesostructure of nano-sized ZSM-5 on the co-cracking of phenolic bio-oil model compounds and ethanol

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Experimental

Materials

Tetraethyl orthosilicate (TEOS, 99.99% metals basis, Aladdin), tetrapropylammonium hydroxide (TPAOH, 40 wt% aqueous solution, Aladdin), tetrapropylammonium bromide (TPABr, 98%, Aladdin), aluminium sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, 99%, Sinopharm), ammonium hydroxide (NH_4OH, 28 wt% aqueous solution, Aladdin), colloidal silica (LUDOX AS-40, 40 wt% aqueous suspension, Sigma-Aldrich), cetyltrimethylammonium bromide (CTAB, 99%, Sinopharm), tetraethylammonium hydroxide (TEAOH, 25 wt% aqueous solution, Aladdin) and hydrochloric acid (HCl, 37 wt%, Sinopharm) were reagents for zeolites synthesis and were used without further purification. Phenol (99%, Sinopharm), guaiacol (98%, Aladdin), eugenol (99%, Aladdin), acetic acid (99.5%, Aladdin), hydroxyacetone (90%, Sigma-Aldrich), 2-methylfuran (98%, Aladdin) and ethanol (99.7%, Sinopharm) were reagents as bio-oil model compounds and were used without further purification.

Characterization

The detailed NH_3-TPD test procedure: the samples were degassed under Ar flow at 300 °C for 2h, followed by saturation at 50 °C for 30 min using 30 mL/min flow of 5% v/v NH_3 in Ar. The sample was then purged at 100 °C under Ar flow for 30 min. NH_3-TPD profiles were subsequently recorded from 100 °C to 600 °C with a heating rate of 10 °C/min.

The detailed Py-IR test procedure: The sample wafers were degassed at 400 °C for 2h in Ar, followed by saturation with pyridine for 30 min at room temperature. The sample was then heated to 150 °C for 1h to let physical adsorbed pyridine evacuated thoroughly. The Py-IR spectra were recorded under room temperature.

X-ray fluorescence (XRF) test was performed on a Thermo ARL 9900 instrument. All samples were dried at 100 °C overnight before test. X-ray photoelectron spectroscopy (XPS) test was performed on a ESCALAB 250Xi instrument with with a focused X-ray source (Al Kα, hv = 1486.6 eV), and the C 1s line was taken as an internal standard at 284.8 eV.

Solid state magic-angle-spinning nuclear magnetic resonance (ssMAS NMR) test was performed on a Bruker Avance III HD instrument equipped with a 3.2 mm MAS probe spinning at 15 kHz. 27Al MAS NMR spectra were recorded with a frequency of 104.24 MHz and a recycle delay of 1 s by using one-pulse sequence. 29Si MAS NMR spectra were recorded with a frequency of 79.49 MHz and a recycle delay of 1.5 s by using cross-polarization (CP) sequence.

Table S1. Detailed acidity properties of all samples.

Sample	C_{BAS}[a,b] (mmol g^{-1})	C_{LAS}[a,b] (mmol g^{-1})	B/L	Total acid amount[b] (mmol g^{-1})
Z	0.086	0.151	0.57	0.238
Z-N	0.266	0.113	2.36	0.378
Z-C	0.233	0.101	2.31	0.334
Z-M	0.138	0.126	1.09	0.265
K1	0.155	0.236	0.66	0.391
K1-N	0.213	0.276	0.77	0.490
K1-C	0.169	0.256	0.66	0.424
K1-M	0.071	0.333	0.21	0.404
K2	0.211	0.223	0.95	0.434
K2-N	0.260	0.244	1.06	0.504
K2-C	0.214	0.197	1.08	0.411
K2-M	0.158	0.269	0.59	0.427

[a] The ratio of concentration of Brønsted to Lewis acid sites (C_{BAS} and C_{LAS}, respectively) were calculated by the Py-IR results.

[b] Total acid amount were calculated by NH_3-TPD results. The quantative value of C_{BAS} and C_{LAS} were obtained by combining the B/L value and total acid amount.

Table S2. Summary for mass yield of liquid, solid and gas products of all samples.

Sample	Aqueous fraction (wt%)	Oil fraction (wt%)	Coke (wt%)	Char (wt%)	Tar (wt%)	Solid[a] (wt%)	Gas (wt%)	Total (wt%)
Z	17.3	22.8	1.2	0.6	3.7	5.5	57.7	103.4
Z-N	16.0	22.0	1.4	0.6	4.9	6.9	49.0	93.9
Z-C	17.6	21.5	1.9	0.5	2.9	5.2	51.0	95.4
Z-M	22.3	17.3	2.8	0.4	1.0	4.3	57.8	101.6
K1	16.1	22.1	1.3	0.6	3.9	5.8	47.5	91.5
K1-N	19.7	22.	1.5	0.8	2.7	4.9	53.0	99.6
K1-C	19.0	19.3	2.6	0.1	2.3	5.0	55.2	98.4
K1-M	19.7	17.2	4.0	0.3	1.8	6.1	49.5	92.5
K2	17.3	23.4	1.4	2.9	1.7	6.0	50.4	97.1
K2-N	21.3	14.3	2.5	0.7	3.6	6.7	59.0	101.3
K2-C	20.1	18.4	3.1	0.5	1.7	5.3	56.6	100.5
K2-M	20.1	17.2	3.9	0.3	1.2	5.4	56.2	98.8

[a]Solid products represent for coke, char and tar products.

Table S3. Detailed product distribution of oil phase fraction presented by selectivity (relative peak area). The unit of all data below is %.

Samples	MAHs (%)	PAHs (%)	Aromatics (%)	Phenol (%)	Guaiacol (%)	Eugenol (%)	Alkylphenol (%)	Phenolics (%)	Oxygenates (%)
Z	8.2	6.3	15.5	27.0	8.4	8.8	23.9	72.9	84.5
Z-N	5.7	5.5	14.8	21.9	11.6	13.2	21.7	73.8	85.2
Z-C	7.8	6.7	19.0	20.2	3.0	2.4	34.1	64.1	81.0
Z-M	17.7	9.3	30.5	20.1	1.2	0.0	41.3	60.3	69.5
K1	8.9	9.3	19.6	24.2	15.3	7.1	19.2	71.3	80.4
K1-N	10.2	8.5	23.1	19.1	4.4	0.8	29.5	58.9	76.9
K1-C	14.7	10.4	29.9	20.9	1.0	0.0	30.9	53.6	70.2
K1-M	22.3	10.9	36.8	17.2	0.0	0.0	40.6	54.7	63.2
K2	12.1	12.4	28.7	26.4	7.0	0.0	24.9	62.3	71.3
K2-N	18.5	10.3	33.6	17.4	0.0	0.0	29.7	51.2	66.5
K2-C	19.6	10.2	36.0	16.8	0.0	0.0	31.2	49.8	64.0
K2-M	21.6	11.5	36.7	17.0	0.0	0.0	40.1	53.8	63.3

Table S4. Detailed product distribution of oil phase fraction presented by relative yield. The unit of all data below is g^{-1}_{feed}.

Samples	MAHs (g^{-1}_{feed})	PAHs (g^{-1}_{feed})	Aromatics (g^{-1}_{feed})	Phenol (g^{-1}_{feed})	Guaiacol (g^{-1}_{feed})	Eugenol (g^{-1}_{feed})	Alkylphenol (g^{-1}_{feed})	Phenolics (g^{-1}_{feed})	Oxygenates (g^{-1}_{feed})
Z	1.9	1.4	3.5	6.2	1.9	2.0	5.5	16.6	19.3
Z-N	1.3	1.2	3.3	4.8	2.6	2.9	4.8	16.3	18.8
Z-C	1.7	1.4	4.1	4.4	0.6	0.5	7.3	13.8	17.4
Z-M	3.1	1.6	5.3	3.5	0.2	0.0	7.1	10.4	12.0
K1	2.0	2.1	4.3	5.3	3.4	1.6	4.2	15.7	17.7
K1-N	2.2	1.9	5.1	4.2	1.0	0.2	6.5	12.9	16.9
K1-C	2.8	2.0	5.8	4.0	0.2	0.0	5.9	10.3	13.5
K1-M	3.8	1.9	6.3	3.0	0.0	0.0	7.0	9.4	10.9
K2	2.8	2.9	6.7	6.2	1.6	0.0	5.8	14.6	16.7
K2-N	2.6	1.5	4.8	2.5	0.0	0.0	4.2	7.3	9.5
K2-C	3.6	1.9	6.6	3.1	0.0	0.0	5.7	9.2	11.8
K2-M	3.8	1.9	6.3	3.0	0.0	0.0	7.1	9.5	11.3

Table S5. The main particle sizes and crystalline sizes of prepared samples.

Sample	Particle size (μm)	Crystalline size[a] (nm)
Z	2.2×0.85	43.4
K1	0.75	36.5
K2	0.25	32.4

[a] Crystalline sizes were calculated through the Scherrer equation.

Table S6. Si/Al ratio of samples obtained by different characterization methods.

Characterization method	Sample	Z	Z-N	K1	K1-N	K2	K2-N
XRF	Si/Al	50	42	48	42	49	45
	Sample	K1	K1-C	K1-M	K2	K2-C	K2-M
XPS	Si/Al	--	42	29	--	36	30
^{29}Si NMR	Si/Al	46	52	36	48	44	33

Table S7. Summary for detailed mass yield of liquid, solid and gas products of all samples during consecutive cycle test.

Samples	Aqueous fraction (wt%)	Oil fraction (wt%)	Tar (wt%)	Solid[a] (wt%)	C_1-C_4 (wt%)	CO (wt%)	CO_2 (wt%)	Gas (wt%)	Total (wt%)
K2	17.3	23.4	1.7	6.0	10.4	22.2	17.7	50.4	97.1
K2_2	18.4	20.8	2.8	6.2	15.8	19.2	14.1	49.1	94.5
K2_3	20.2	15.9	1.4	4.2	25.9	19.5	11.3	56.7	97.0
K2_4	22.5	15.8	2.1	4.4	24.6	18.8	12.6	56.0	98.7
K2-M	20.1	17.2	1.2	5.3	24.8	28.3	3.0	56.2	98.8
K2-M_2	21.2	14.3	1.5	4.5	35.7	22.4	3.0	61.1	101.0
K2-M_3	21.5	15.9	1.6	4.9	33.9	21.9	2.4	58.3	100.6
K2-M_4	21.7	13.7	1.6	4.9	33.5	20.9	2.3	56.7	96.9
K1-M	19.7	17.2	1.8	6.4	19.1	27.1	3.2	49.5	92.9
K1-M_2	20.0	11.9	1.8	5.7	29.0	24.2	3.9	57.1	94.6
K1-M_3	21.5	14.6	1.6	5.5	31.1	24.3	2.9	58.3	99.9
K1-M_4	21.2	14.4	1.0	4.6	30.3	23.2	4.5	58.0	98.2

[a]Solid products represent for coke, char and tar products.

Table S8. Detailed product distribution of oil phase fraction during consecutive cycle test. The unit of all data below is g^{-1}_{feed}.

Samples	MAHs (g^{-1}_{feed})	Aromatics (g^{-1}_{feed})	PAHs/Aromatics	Alkylphenol (g^{-1}_{feed})	Phenolics (g^{-1}_{feed})	Oxygenates (g^{-1}_{feed})
K2	2.8	6.7	0.43	5.8	14.6	16.7
K2_2	2.7	5.0	0.36	6.5	13.5	15.7
K2_3	2.2	4.2	0.37	5.9	10.0	11.7
K2_4	1.5	3.3	0.44	6.3	10.9	12.5
K2_M	3.8	6.3	0.30	7.1	9.5	11.3
K2-M_2	3.8	4.9	0.19	5.7	8.4	9.4
K2-M_3	3.4	4.4	0.18	6.4	10.1	11.5
K2-M_4	2.9	3.9	0.21	5.3	9.0	9.8
K1-M	3.8	6.3	0.30	7.0	9.4	10.9
K1-M_2	3.6	5.2	0.23	4.2	6.1	6.6
K1-M_3	3.2	4.3	0.21	5.9	9.7	10.2
K1-M_4	2.9	4.0	0.23	5.9	9.4	10.4

Table S9. Major identified compounds (>0.5 %, relative peak area) in the oil phase fraction of the upgraded bio-oil by GC/MS. 2-Methylfuran, acetic acid and 1-Hydroxy-2-propanone haven't been found in all upgraded samples, and are listed below for reference, noted as Reactants.

RT / min	Compound name	Formula	Category
3.5	2-Methylfuran	C_5H_6O	Reactants
4.4	Benzene	C_6H_6	BTEX
6.63	Toluene	C_7H_8	BTEX
8.92	Ethylbenzene	C_8H_{10}	BTEX
9.13	o-Xylene	C_8H_{10}	BTEX
9.32	p-Xylene	C_8H_{10}	BTEX
10.52	o-Xylene	C_8H_{10}	BTEX
11.62	1-Ethyl-3-methyl-benzene	C_9H_{12}	MAHs
11.69	1-Ethyl-3-methyl-benzene	C_9H_{12}	MAHs
12.04	1-Ethyl-2-methyl-benzene	C_9H_{12}	MAHs
12.16	1-Ethyl-3-methyl-benzene	C_9H_{12}	MAHs
13.25	1,2,4-Trimethyl-benzene	C_9H_{12}	MAHs
13.81	1-Hydroxy-2-propanone	$C_3H_6O_2$	Reactants
15.68	Indane	C_9H_{10}	Aromatics
16.21	1-Methyl-2-(1-methylethyl)-benzene	$C_{10}H_{14}$	MAHs
16.62	1,1,1-Trimethoxy-ethane	$C_5H_{12}O_3$	Oxygenates
17.73	Acetic acid	$C_2H_4O_2$	Reactants
18.14	1-(Acetyloxy)-2-propanone	$C_5H_8O_3$	Oxygenates
18.63	Indene	C_9H_8	Aromatics
18.65	2-Ethenyl-1,4-dimethyl-benzene	$C_{10}H_{12}$	MAHs
19.15	Benzofuran	C_8H_6O	Oxygenates
20.66	2,3-Dihydro-2-methyl-benzofuran	$C_9H_{10}O$	Oxygenates
20.8	1,2,4,5-Tetramethyl-benzene	$C_{10}H_{14}$	MAHs
21.05	1,4-Dihydronaphthalene	$C_{10}H_{10}$	Aromatics
21.36	2-Methyl-benzofuran	C_9H_8O	Oxygenates
21.64	1-Methyl-1H-indene	$C_{10}H_{10}$	Aromatics
23.28	2-Hydroxy-benzaldehyde	$C_7H_6O_2$	Oxygenates
23.41	1,1-Dimethyl-1H-indene	$C_{11}H_{12}$	Aromatics
23.81	4,7-Dimethyl-benzofuran	$C_{10}H_{10}O$	Oxygenates
23.98	2,3-Dihydro-4,7-dimethyl-1H-indene	$C_{11}H_{14}$	Aromatics
24.12	4-(5-Methyl-2-furyl)butan-2-one	$C_9H_{12}O_2$	Oxygenates
24.4	2,2'-Ethylidenebis(5-methylfuran)	$C_{12}H_{14}O_2$	Oxygenates
24.7	Naphthalene	$C_{10}H_8$	PAHs
25.83	2,3-Dihydro-4,5,7-trimethyl-1H-indene	$C_{12}H_{16}$	Aromatics
26.02	2-Methyl-6-(2-propenyl)-phenol	$C_{10}H_{12}O$	Alkyl phenols
27.13	2-Methyl-naphthalene	$C_{11}H_{10}$	PAHs
27.3	Guaiacol	$C_7H_8O_2$	Guaiacol
29.06	2-Ethyl-naphthalene	$C_{12}H_{12}$	PAHs
29.2	1-Methyl-naphthalene	$C_{11}H_{10}$	PAHs

29.26	2-Methoxy-4-methyl-phenol	$C_8H_{10}O_2$	Phenolics
29.4	1,7-Dimethyl-naphthalene	$C_{12}H_{12}$	PAHs
29.54	1-(1-Methylethyl)-naphthalene	$C_{13}H_{14}$	PAHs
30.24	Phenol	C_6H_6O	Phenol
30.44	2-Hydroxy-3-(2-propenyl)-benzaldehyde	$C_{10}H_{10}O_2$	Phenolics
30.83	4-Ethyl-2-methoxy-phenol	$C_9H_{12}O_2$	Phenolics
31.23	1,4,5-Trimethyl-naphthalene	$C_{13}H_{14}$	PAHs
31.5	2-Ethyl-phenol	$C_8H_{10}O$	Alkyl phenols
31.61	2,5-Dimethyl-phenol	$C_8H_{10}O$	Alkyl phenols
31.69	3-Methyl-phenol	C_7H_8O	Alkyl phenols
31.82	3-Methyl-phenol	C_7H_8O	Alkyl phenols
33.08	2-Ethyl-5-methyl-phenol	$C_9H_{12}O$	Alkyl phenols
33.16	4-Ethyl-phenol	$C_8H_{10}O$	Alkyl phenols
33.26	3-Ethyl-phenol	$C_8H_{10}O$	Alkyl phenols
33.43	2-Methoxy-3-(2-propenyl)-phenol	$C_{10}H_{12}O_2$	Phenolics
33.53	3,5-Diethyl-phenol	$C_{10}H_{14}O$	Alkyl phenols
33.68	3,4-Dimethyl-phenol	$C_8H_{10}O$	Alkyl phenols
34.05	2-Methyl-5-(1-methylethyl)-phenol	$C_{10}H_{14}O$	Alkyl phenols
34.18	2-Ethyl-5-methyl-phenol	$C_9H_{12}O$	Alkyl phenols
34.26	2-Methoxy-4-(1-propenyl)-, (Z)-phenol	$C_{10}H_{12}O_2$	Phenolics
34.34	2,2'-Isopropylidenebis(5-methylfuran)	$C_{13}H_{16}O_2$	Phenolics
34.58	2-Methoxy-6-(1-propenyl)-phenol	$C_{10}H_{12}O_2$	Phenolics
34.67	2-Methyl-6-(2-propenyl)-phenol	$C_{10}H_{12}O$	Alkyl phenols
34.71	Eugenol	$C_{10}H_{12}O_2$	Eugenol
35.36	Eugenol	$C_{10}H_{12}O_2$	Eugenol
35.42	Phthalan	C_8H_8O	Oxygenates
35.46	2,3-Dihydro-1H-indenol	$C_9H_{10}O$	Oxygenates
35.63	Eugenol	$C_{10}H_{12}O_2$	Eugenol
35.7	2-Methyl-6-(2-propenyl)-phenol	$C_{10}H_{12}O$	Alkyl phenols
36.07	1-Methyl-3-(phenylmethyl)-benzene	$C_{14}H_{14}$	PAHs
36.34	4-(2-Propenyl)-phenol	$C_9H_{10}O$	Alkyl phenols
36.48	2-Ethyl-benzaldehyde	$C_9H_{10}O$	Oxygenates
36.87	2-Methyl-6-(2-propenyl)-phenol	$C_{10}H_{12}O$	Alkyl phenols
36.99	2-Methyl-6-(2-propenyl)-phenol	$C_{10}H_{12}O$	Alkyl phenols
37.9	1H-Indenol	C_9H_8O	Oxygenates
39.19	1,2-Benzenediol	$C_6H_6O_2$	Oxygenates
39.54	Hydroquinone	$C_6H_6O_2$	Phenolics
39.79	Anthracene	$C_{14}H_{10}$	PAHs
40.17	4-Methyl-1,2-benzenediol	$C_7H_8O_2$	Oxygenates
43.76	2-Naphthalenol	$C_{10}H_8O$	Oxygenates
45.77	2-Methyl-1-naphthalenol	$C_{11}H_{10}O$	Oxygenates
45.96	2-Methyl-1-naphthalenol	$C_{11}H_{10}O$	Oxygenates
46.05	1,4-Naphthalenedione	$C_{10}H_6O_2$	Oxygenates

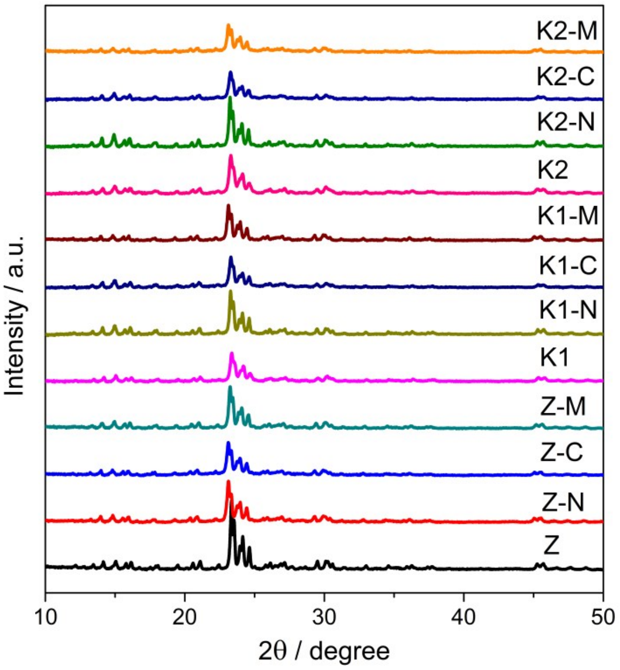

Figure S1. XRD patterns of all samples.

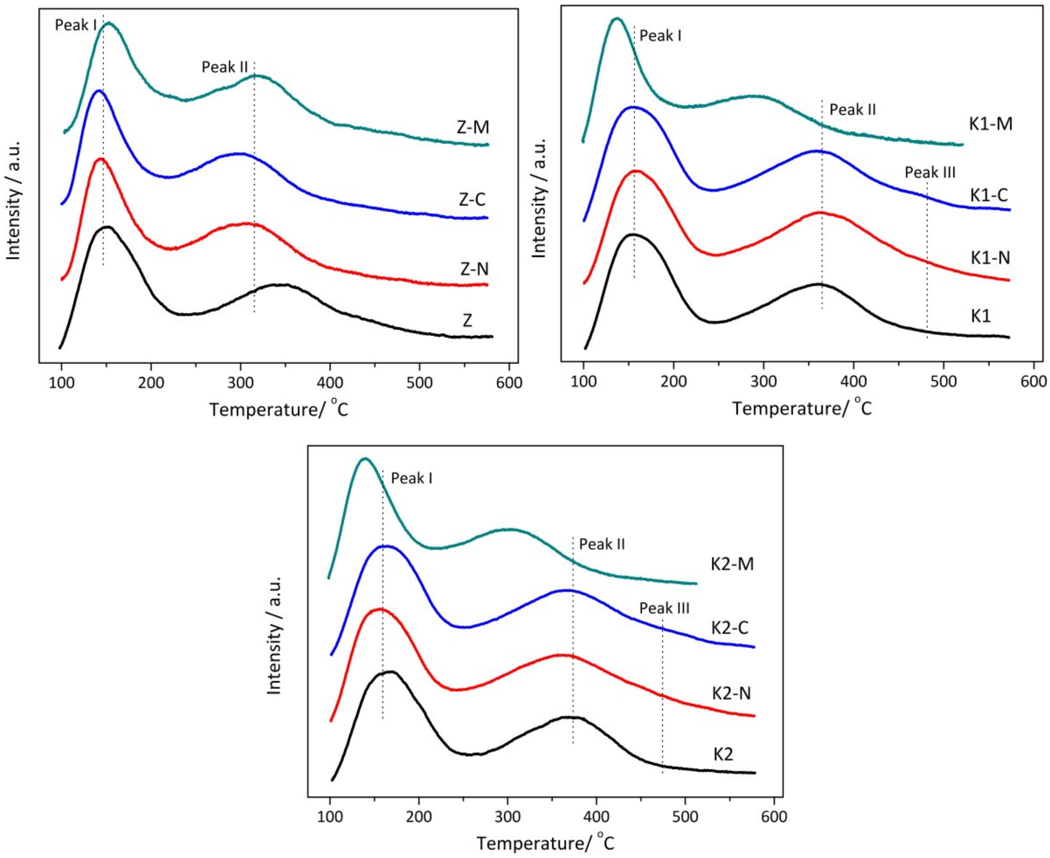

Figure S2. NH_3-TPD profiles of all samples. a) Micron size ZSM-5; b) 750nm size ZSM-5; c) 250nm size ZSM-5. Peak I and Peak II are assigned to the weak and strong acid sites, respectively. And Peak III represents for the additional acid sites with stronger acidity caused by the ammonia hydrothermal treatment.

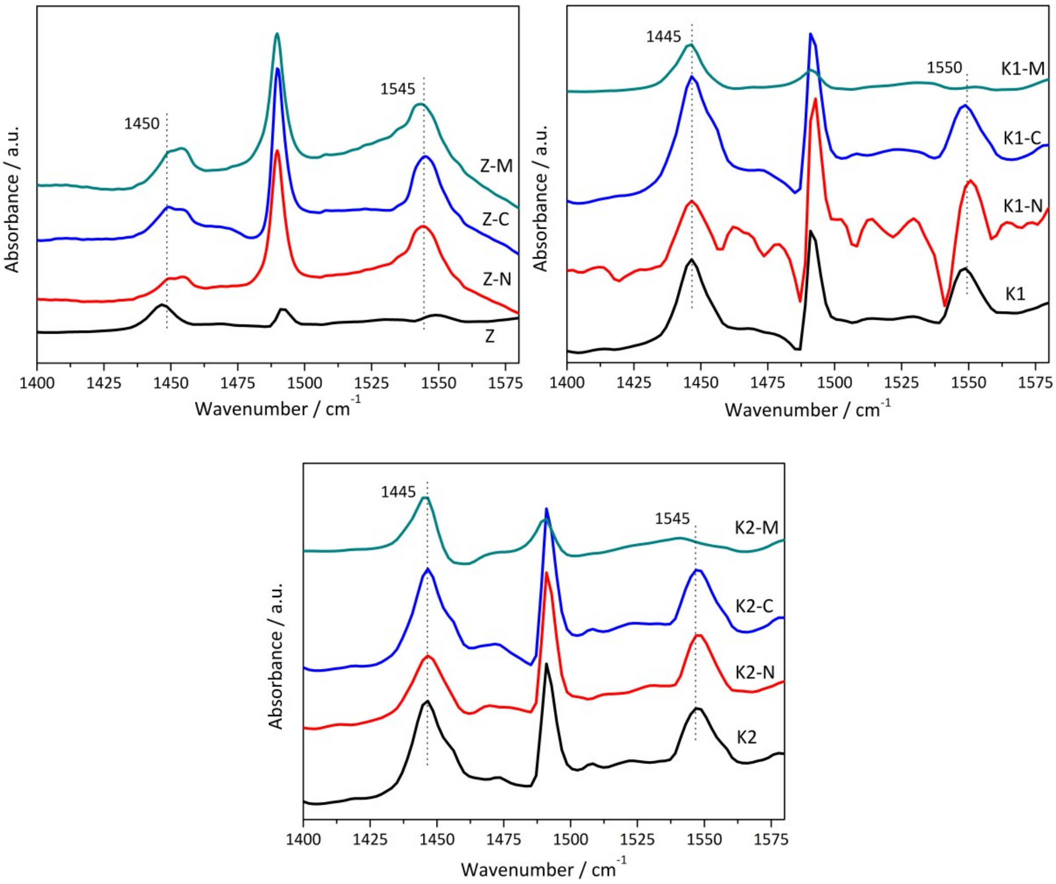

Figure S3. Py-IR spectras of all samples. a) Micron size ZSM-5; b) 750nm size ZSM-5; c) 250nm size ZSM-5. The peaks at 1445cm^{-1} and 1545cm^{-1} are assigned to the absorption of pyridine on the Lewis and Brønsted acid sites, respectively.

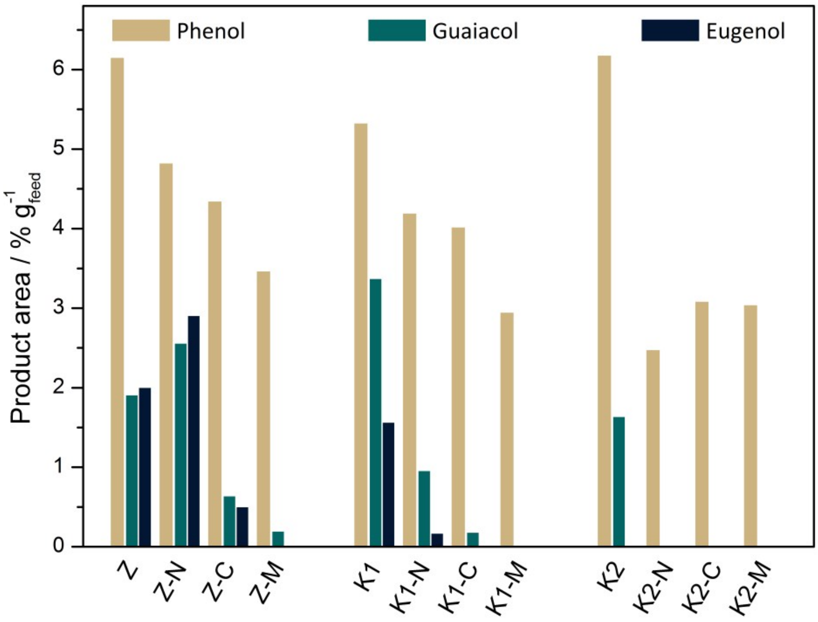

Figure S4. Relative yield of three phenolic reactants: phenol, guaiacol and eugenol.

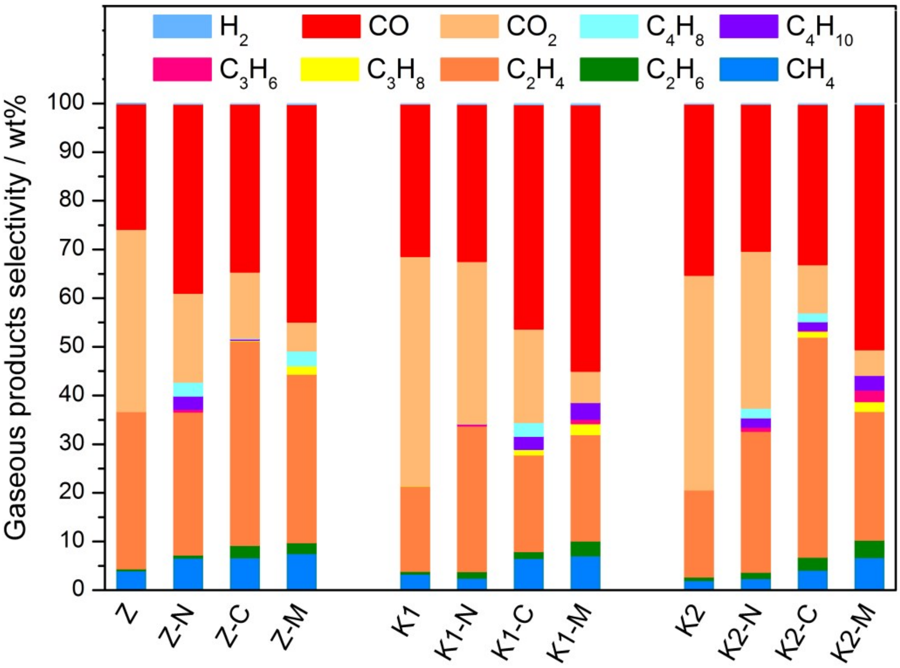

Figure S5. Detailed gaseous product selectivity of all samples.

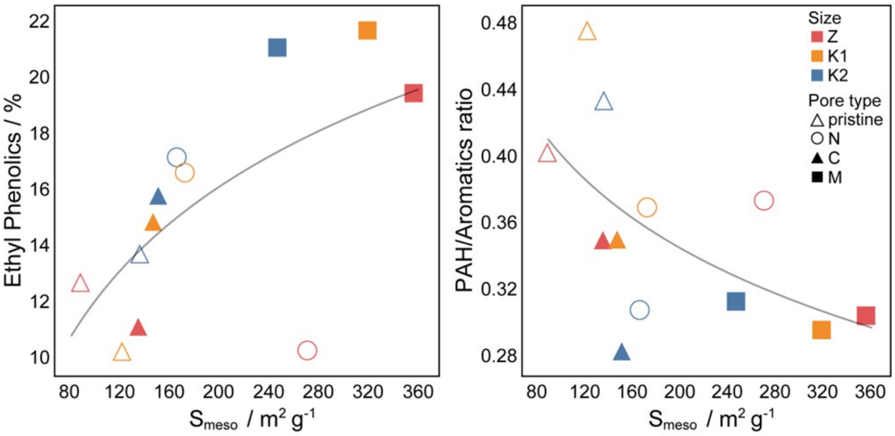

Figure S6. Correlation between S_{meso} and a) selectivity of ethyl phenolics (relative peak area); b) ratio of PAHs to aromatics.

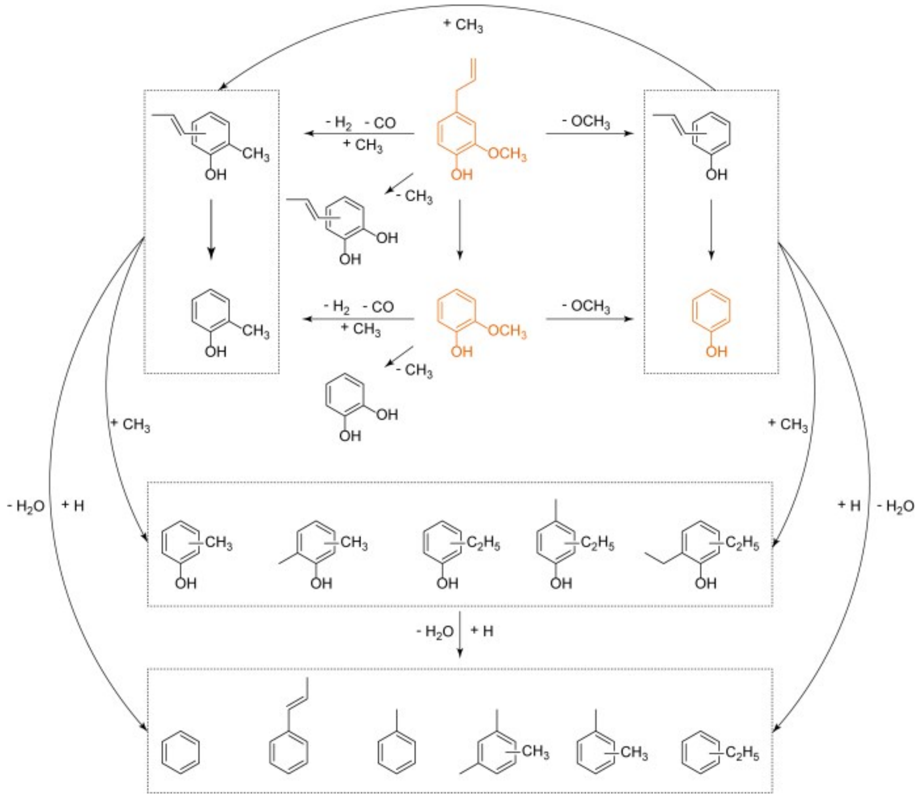

Figure S7. Primary conversion routes for phenol, guaiacol and eugenol during co-cracking with ethanol.

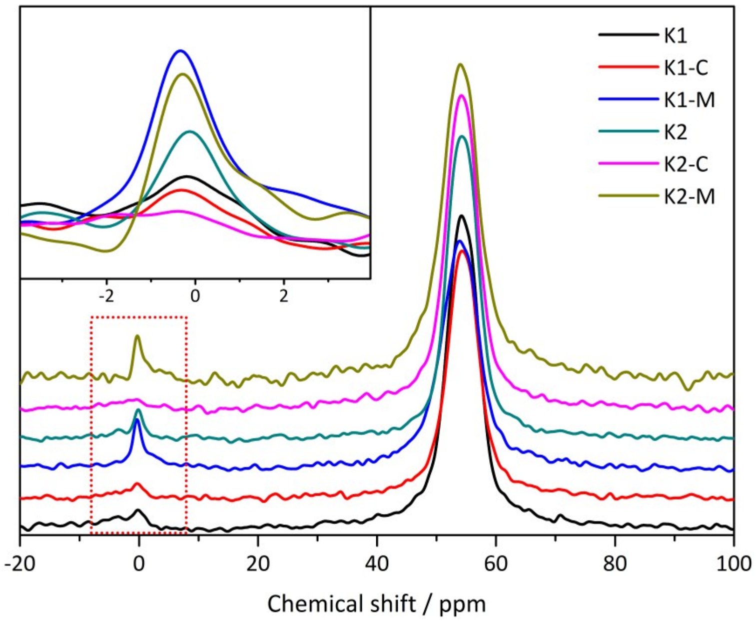

Figure S8. ^{27}Al ssMAS NMR spectras of nano samples. Inset is the magnification of marked area, and spectras are stacked with the same baseline.

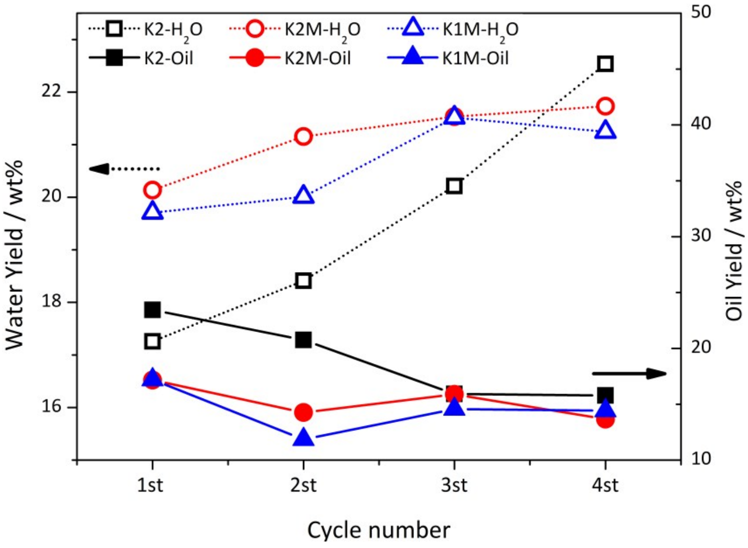

Figure S9. Yield of water phase and oil phase product of all three catalysts during the consecutive cycle test.

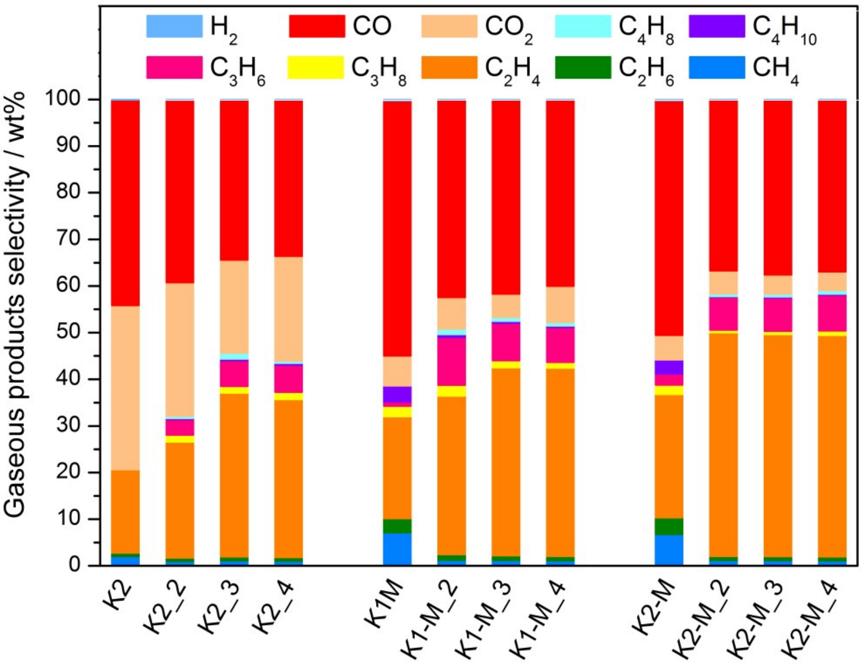

Figure S10. Detailed gaseous product selectivity of three catalysts during the consecutive cycle test.