Electronic Supplementary Information

Direct conversion of cellulose and raw biomass to acetonitrile by catalytic fast pyrolysis in ammonia

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Contents

Experimental details

1. Materials

Acetonitrile (AR), xylene (AR), toluene (AR), benzene(AR) and methanol (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. Pyrrole (AR), 2-methylpyridine (AR), 3-methylpyridine (AR), 4-methylpyridine (AR), indole(AR), pyridine (AR) and bicyclohexane (AR) were purchased from Aladdin Chemical Reagent Co. Ltd.

Metal nitrates including $Co(NO_3)_2 \cdot 6H_2O$ (99%), $Fe(NO_3)_3 \cdot 9H_2O$ (98.5%), $Ni(NO_3)_2 \cdot 6H_2O$ (98%), $Cu(NO_3)_2 \cdot 3H_2O$ (99%) and $Zn(NO_3)_2 \cdot 6H_2O$ (99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. SiO_2, γ-Al_2O_3, β-zeolite (Si/Al = 25), MCM-41, USY (25), and HZSM-5 with different Si/Al ratios (Si/Al = 25, 50, 80) were purchased from Catalyst Plant of Nankai University. All these chemicals were used without further purification. N_2 (99.999%), NH_3 (99.995%), Ar (99.999%) and standard gases such as CH_4, C_2H_4, C_2H_6, CO, CO_2, H_2, were purchased from Nanjing Special Gases Factory.

Cellulose was purchased from Aladdin Chemical Reagent Co. Ltd. De-alkali lignin was purchased from Beijing Bailingwei Technology Co., Ltd. Xylose was purchased from Sinopharm Chemical Reagent Co. Ltd. Bagasse, rice husk, and birch were purchased from Guangxi Guigang Ganhua Inc., China.

2. Catalyst characterization

X-ray photoelectron spectroscopy (XPS) spectra were obtained using an X-ray photoelectron spectrometer (ESCALAB250).

Elemental analysis was measured using an Elementar vario EL cube. The combustion tube temperature was 950°C, and the reducing tube temperature was 550°C.

Hydrogen temperature-programmed reduction (H_2-TPR) was carried out in a home-

[1] Ma, Y. F., Xu, G. Y., Wang, H., Zhang, Y. & Fu, Y. Cobalt Nanocluster Supported on ZrREnOx for the Selective Hydrogenation of Biomass Derived Aromatic Aldehydes and Ketones in Water. *ACS Catal.* **8**, 1268-1277 (2018).

built reactor system coupled to a gas chromatograph. The details can be seen in reference [1].

XRD analysis was conducted on an X-ray diffractometer (TTR-III, Rigaku Corp., Japan) using Cu Kα radiation (λ = 1.54056 Å) at 40 kV and 40 mA. The data were recorded over a 2θ range of 10−70°. The sample after reaction was dried at 40°C after filtration and acetone sequential washing

Pyridine-IR characterization was performed on a Nicolet iS50 FT-IR Spectrometer. The samples were prepared based on KBr pellettechnique. Prior to pyridine adsorption at room temperature for 1 h, each sample was treated under vacuum at 400°C for 3 h. The unabsorbed pyridine was removed by a vacuum pump. The obtained sample was then subjected to desorption procedure. At a desorption temperature of 200°C, the spectra were recorded for further analysis.

We used inductively coupled plasma-atomic absorption spectroscopy (ICP-AAS, PerkinElmer Corporation AA800) to quantify the Co species by treating 100 mg of the catalyst in 20 ml of 2 mol/L HCl at 25 °C for 24 hours. CoOx on the surface of the catalyst can be dissolved, while Co species in the HZSM-5 skeleton will be retained.

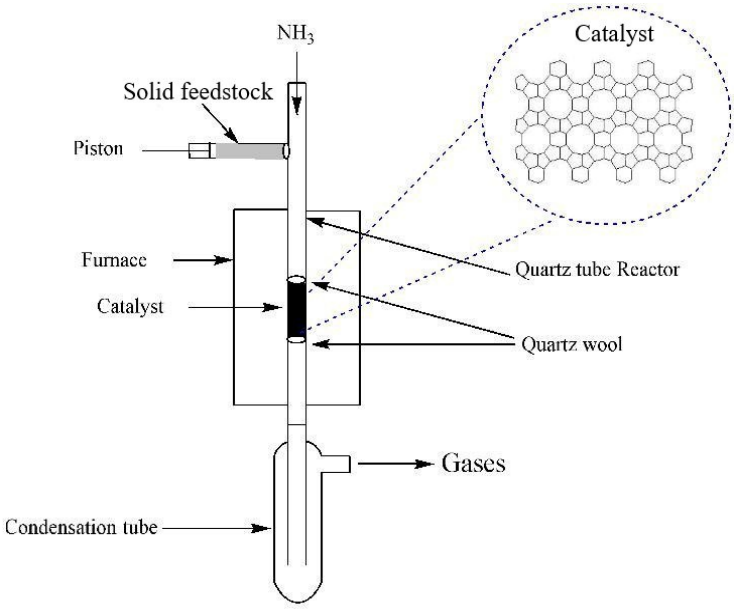

Fig. S1 Scheme of bench-top device for solid feedstock CFP-A

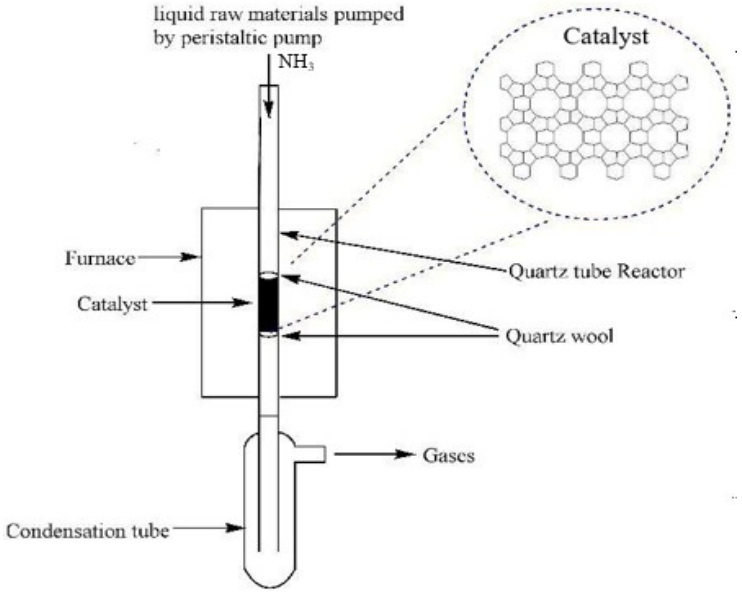

Fig. S2 Scheme of bench-top device for liquid raw materials CFP-A

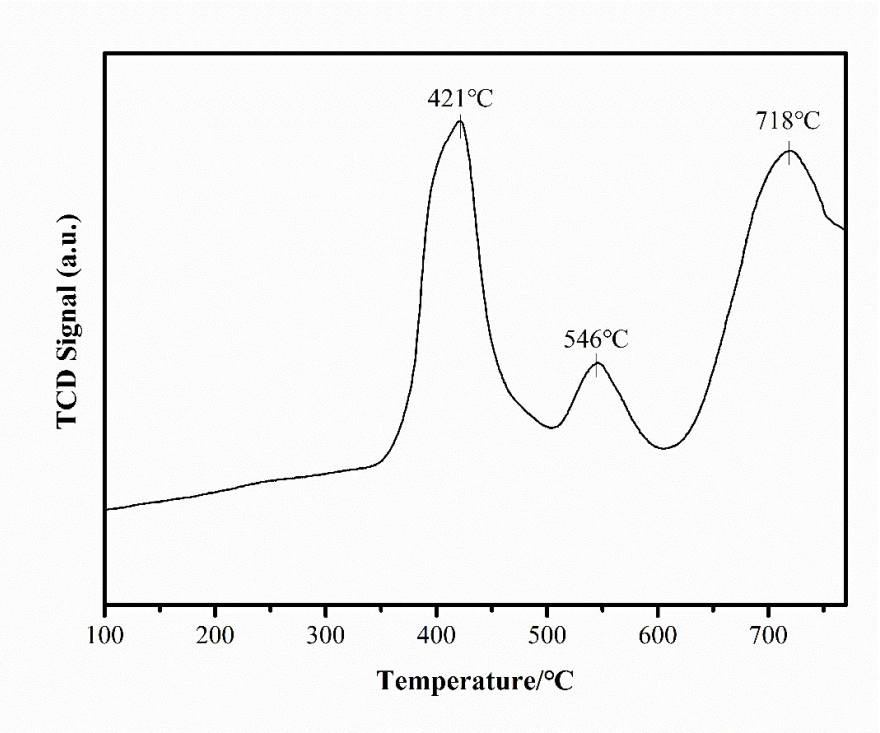

Fig. S3 H_2-TPR profile for CoOx/HZSM-5 catalyst.

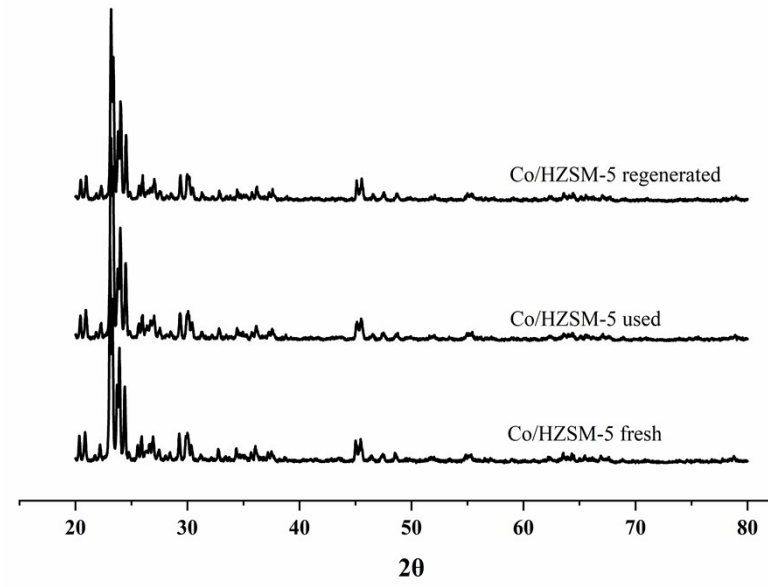

Fig. S4 XRD patterns of the catalysts

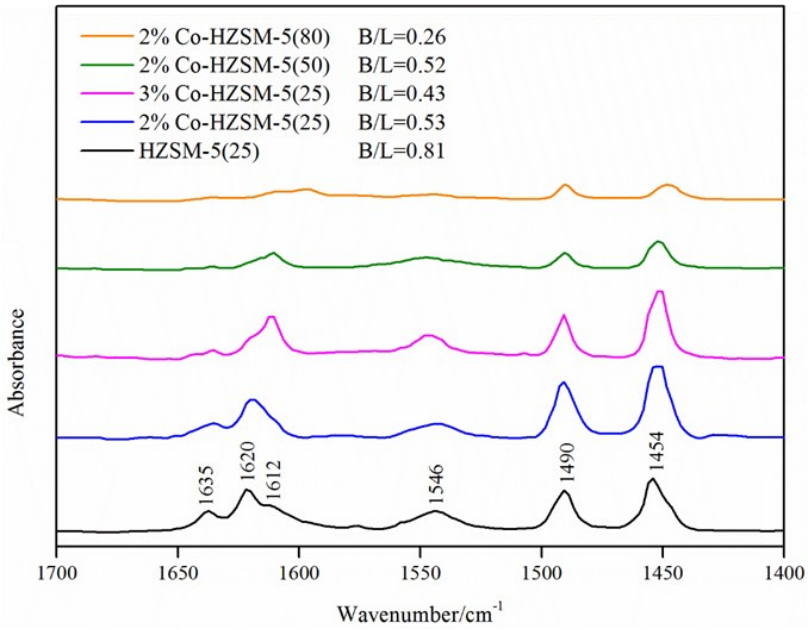

Fig. S5 Pyridine-IR spectra of the catalysts at 200 °C

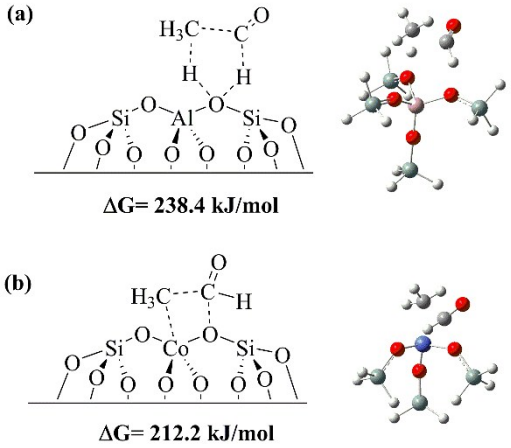

Fig. S6 Promoted breakage of C-C bond of acetaldehyde by HZSM-5 (a) and CoOx/HZSM-5 catalyst (b), calculated at B3LYP/6-311G(d,p) level.

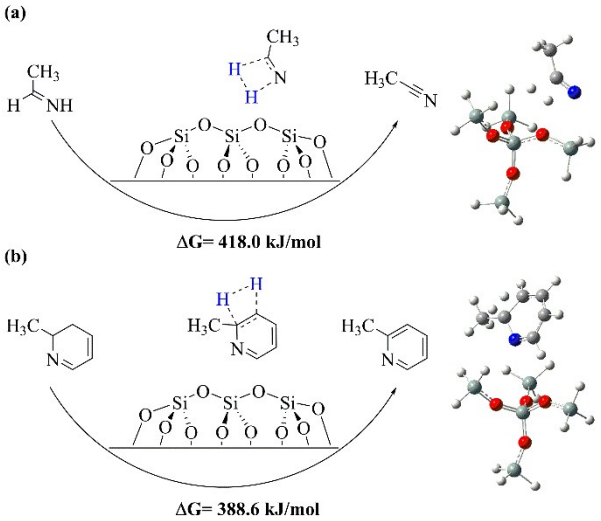

Fig. S7 Dehydrogenation reactions for acetonitrile formation (a) and 2-methylpyridine formation (b) at indigenous L acid site (Si), calculated at B3LYP/6-311G(d,p) level

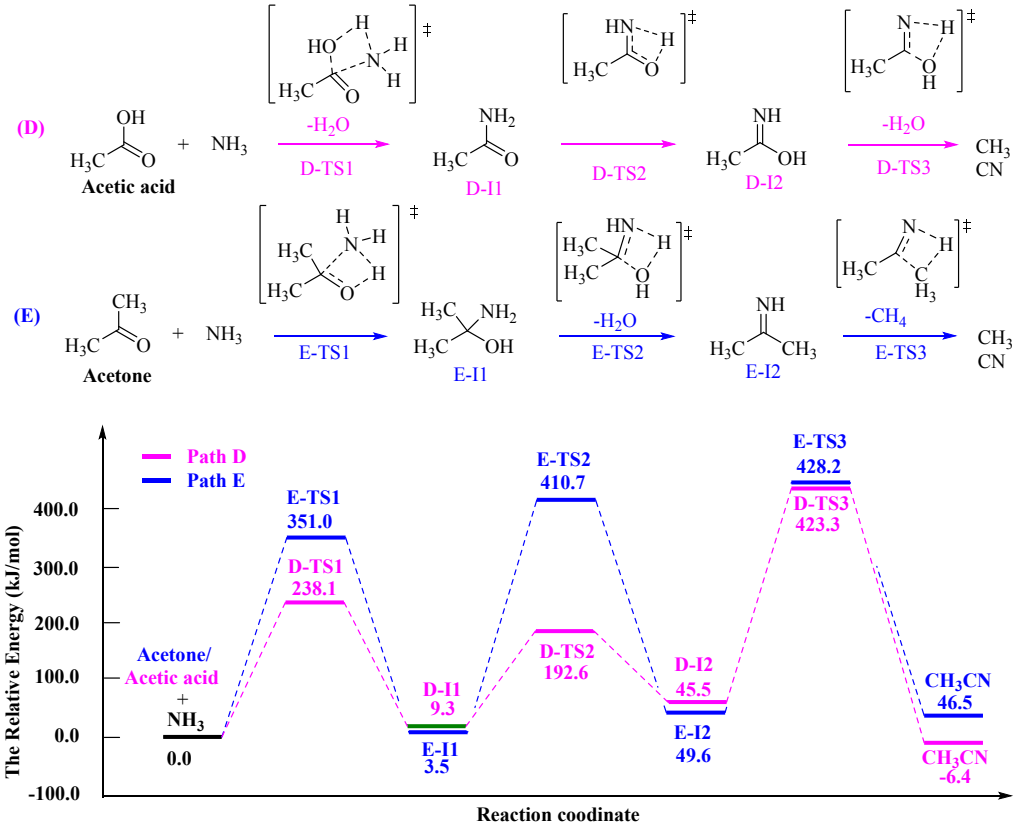

Fig. S8 Evolution pathways and energy diagrams for acetonitrile formation from acetic acid and acetone

Table S1 Effect of doped mental on the performance of the HZSM-5(25) based catalyst

Catalyst (M/HZSM)	Co	Ni	Fe	Cu	Zn	HZSM-5
Total carbon yield	95.99	91.00	87.11	91.07	93.33	76.69
Bio-oil	34.53	17.82	34.31	30.88	20.18	16.00
Coke	21.11	24.93	21.08	46.32	39.96	39.59
Gases	40.35	48.25	31.72	13.87	33.19	21.1
Detected products in the organic bio-oil (C%)						
Acetonitrile	28.73	13.89	22.18	17.19	15.65	5.25
Aromatics	3.93	2.95	3.76	4.31	2.84	3.15
Pyridines	0.83	0.48	2.97	7.71	1.69	5.64
Pyrroles	0.80	0.19	2.76	0.18	0.00	0.73
Indoles	0.24	0.31	2.64	1.49	0.00	1.23
Detected products Selectivity (%)						
Acetonitrile	83.20	77.95	64.65	55.67	77.55	32.81
Aromatics	11.38	16.55	10.96	13.96	14.07	19.69
Pyridines	2.40	2.69	8.66	24.97	8.37	35.25
Pyrroles	2.32	1.74	8.04	0.58	0.00	4.56
Indoles	0.70	0.70	7.69	4.83	0.00	7.69

Conditions: Temperature, 650 °C; Catalyst, M/HZSM-5, Si/Al = 25, metal loading 2%, 1 g; NH_3 flow rate 80 mL/min.

Table S2 Effect of different support on the catalytic performance.

Co/support	Co/HZ-5(25)	Co/HZ-5(50)	Co/HZ-5(80)	Co/γAl_2O_3	Co/mcm-41	Co/USY	Co/Hβ(25)	Co/MgO	Co/SiO_2
Total carbon yield (C %)	95.99	95.12	92.25	85.50	84.12	87.30	86.51	85.70	85.42
Bio-oil	34.53	33.90	30.65	15.42	17.35	17.37	24.63	12.07	10.08
Coke	21.11	20.00	18.34	20.56	15.84	34.04	21.21	33.20	24.58
Gases	40.35	41.22	43.26	49.52	50.93	35.89	40.65	40.88	50.76
Detected products in the organic bio-oil (C%)									
Acetonitrile	28.73	22.51	12.61	14.28	10.97	12.12	13.04	6.40	8.60
Aromatics	3.93	2.30	2.92	0.11	2.18	2.54	3.83	2.49	0.23
Pyridines	0.83	4.40	6.22	0.48	2.78	2.63	3.02	0.67	0.51
Pyrroles	0.80	4.69	8.90	0.55	1.41	0.08	4.74	1.70	0.74
Indoles	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.36	0.00
Detected products Selectivity (%)									
Acetonitrile	83.20	66.40	41.14	92.61	63.23	69.78	52.94	53.02	85.32
Aromatics	11.38	6.78	9.53	0.71	12.56	14.62	15.55	20.62	2.28
Pyridines	2.40	12.98	20.29	3.11	16.02	15.14	12.26	5.55	5.06
Pyrroles	2.32	13.83	29.04	3.57	8.13	0.46	19.24	14.08	7.34
Indoles	0.70	0.00	0.00	0.00	0.00	0.00	0.00	2.98	0.00

Conditions: Temperature, 650 °C; Catalyst, Co/support, cobalt loading 2%, dosage, 1 g; NH_3 flow 80ml/min.

Table S3 Effect of different loading on the catalytic performance

Loading （%）	0	1	2	3	4	5
Total carbon yield (C %)	76.69	88.66	95.99	91.70	90.56	89.90
Bio-oil	16.00	25.77	34.53	38.40	33.00	31.38
Coke	39.59	29.03	21.11	16.39	9.49	7.31
Gases	21.1	33.85	40.35	40.91	47.73	50.88
Detected products in the organic bio-oil (C%)						
Acetonitrile	5.25	20.73	28.73	32.48	26.72	25.40
Aromatics	3.15	3.17	3.93	3.72	3.76	3.39
Pyridines	0.64	0.83	0.83	0.99	1.48	1.48
Pyrroles	0.73	0.80	0.80	1.21	1.04	1.11
Indoles	1.23	0.24	0.24	0.00	0.00	0.00
Detected products Selectivity (%)						
Acetonitrile	47.73	80.44	83.20	84.58	80.96	80.94
Aromatics	28.64	12.30	11.38	9.69	11.39	10.80
Pyridines	5.82	3.22	2.40	2.58	4.48	4.71
Pyrroles	6.64	3.10	2.32	3.15	3.15	3.54
Indoles	11.18	0.93	0.70	0.00	0.00	0.00

Conditions: Temperature, 650 °C; Catalyst, HZSM-5, Si/Al = 25, dosage, 1 g; NH_3 flow rate 80 mL/min.

Table S4 Effect of reaction temperature on product distribution

Temperature (°C)	550	600	650	700
Total carbon yield (C %)	84.07	93.86	92.70	90.78
Bio-oil	23.54	43.49	35.40	24.86
Coke	31.67	18.47	16.39	12.04
Gases	28.86	31.90	40.91	53.88
Detected products in the organic bio-oil (C%)				
Acetonitrile	18.88	34.36	28.48	19.69
Aromatics	2.37	3.38	3.72	2.94
Pyridines	1.02	2.45	1.99	1.03
Pyrroles	1.27	2.51	1.21	1.00
Indoles	0.00	0.79	0.00	0.20
Acetonitrile	80.20	79.01	80.45	79.20
Aromatics	10.07	7.77	10.50	11.83
Pyridines	4.33	5.63	5.62	4.14
Pyrroles	5.40	5.77	3.42	4.03
Indoles	0.00	1.82	0.00	0.80

Conditions: Catalyst, Co/HZSM-5, cobalt loading 3%, Si/Al = 25, dosage, 1 g; NH_3 flow rate, 80 mL/min.

Table S5 Effect of different resident time on product distribution

Time (s)	0.88	1.32	1.77	2.65	3.53
Total carbon yield (C %)	81.71	92.08	93.89	89.72	89.48
Bio-oil	28.77	34.74	43.50	32.80	24.00
Coke	35.47	31.67	18.47	18.75	18.56
Gases	17.47	25.67	31.91	38.17	45.92
Detected products in the organic bio-oil (C%)					
Acetonitrile	15.23	23.48	34.36	28.33	21.44
Aromatics	2.71	3.73	3.38	2.72	1.51
Pyridines	2.17	2.97	2.46	0.85	1.05
Pyrroles	2.96	3.37	2.51	0.45	0.00
Indoles	5.70	1.19	0.79	0.45	0.00
Detected products Selectivity (%)					
Acetonitrile	52.94	67.59	78.99	86.37	89.33
Aromatics	9.42	10.74	7.77	8.29	6.29
Pyridines	7.54	8.55	5.66	2.60	4.38
Pyrroles	10.29	9.70	5.77	1.37	0.00
Indoles	19.81	3.43	1.82	1.37	0.00

Conditions: Temperature, 600 °C; Catalyst, Co/HZSM-5, cobalt loading 3%, Si/Al = 25; NH_3 flow rate 80 mL/min.

Table S6 Effect of different NH_3 flow rate on product distribution

NH3 flow rate(ml/min)	40	60	80	100	120
Total carbon yield (C %)	80.16	88.85	93.89	86.98	82.93
Bio-oil	23.29	37.70	43.51	36.32	31.76
Coke	29.39	22.27	18.47	18.28	18.05
Gases	27.48	28.88	31.91	32.38	33.12
Detected products in the organic bio-oil (C%)					
Acetonitrile	18.67	29.74	34.36	25.94	22.83
Aromatics	2.10	2.88	3.38	4.21	3.24
Pyridines	1.05	2.20	2.46	2.67	2.62
Pyrroles	1.12	2.31	2.51	3.18	2.88
Indoles	0.35	0.57	0.79	0.32	0.19
Detected products Selectivity (%)					
Acetonitrile	80.16	78.89	78.97	71.42	71.88
Aromatics	9.02	7.64	7.77	11.59	10.20
Pyridines	4.51	5.93	5.62	7.35	8.25
Pyrroles	4.81	6.13	5.76	8.76	9.07
Indoles	1.50	1.51	1.82	0.88	0.60

Conditions: Temperature, 600 °C; Catalyst, Co/HZSM-5, cobalt loading 3%, Si/Al = 25, dosage, 1 g.

Table S7 Product distribution of different feedstock under optimal condition

Feedstock	Bagasse	Rice husk	Birch	Lignin	Xylose
Total carbon yield (C %)	88.57	85.43	85.62	89.33	87.04
Bio-oil	16.38	15.48	17.05	10.22	13.29
Coke	50.92	43.97	40.88	68.82	36.33
Gases	21.27	25.98	27.69	18.29	37.42
Detected products in the organic bio-oil (C%)					
Acetonitrile	12.81	11.58	11.05	4.37	8.57
Aromatics	1.26	2.33	2.13	2.05	2.39
Pyridines	1.58	0.58	3.16	1.74	2.33
Pyrroles	0.73	0.99	0.72	0.00	1.58
Indoles	0.00	0.00	0.00	2.06	0.00
Detected products Selectivity (%)					
Acetonitrile	78.19	74.48	64.78	42.76	64.48
Aromatics	7.68	15.06	12.48	20.05	17.98
Pyridines	9.66	3.73	18.55	17.03	17.53
Pyrroles	4.47	6.37	4.20	0.00	11.89
Indoles	0.00	0.00	0.00	20.16	0.00

Conditions: Temperature, 600 °C; Co/HZSM-5, cobalt loading 3%, Si/Al = 25, dosage 1 g; NH_3 flow rate 80ml/min.

Table S8 Product distribution of cellulose pyrolysis under nitrogen

Detected compounds	Resident time	Peak area	
		HZSM-5	Co-HZSM-5
Acetaldehyde	1.61	2.84E+07	1.60E+07
Furan	1.74	5.73E+06	5.36E+06
Acetone	1.78	1.26E+07	7.47E+06
Acetic acid	2.05	1.14E+07	3.05E+06
HAA	2.16	8.65E+07	5.68E+07
Acetol	2.68	9.07E+07	4.74E+07
Methyl furan	4.44	1.85E+07	1.07E+07
Benzene	2.41	2.19E+08	1.89E+08
Toluene	3.14	4.70E+08	3.92E+08
Xylene	4.07	6.08E+08	3.97E+08
Naphthalene	8.07	2.77E+08	2.78E+08
1-methyl-naphthalene	9.06	2.76E+08	1.95E+08
LG	11.89	9.81E+08	1.37E+09

Conditions: Temperature, 600 °C; Carrier gas, N_2

Atom coordinates of optimized geometries for all the compounds calculated at B3LYP/6-311G(d,p) level

Acetaldehyde

C	-1.16886300	-0.14786500	-0.00000200
H	-1.70775900	0.22284400	-0.87874900
H	-1.70724700	0.22256700	0.87920500
H	-1.15578600	-1.23752900	-0.00020300
C	0.23557400	0.39712500	-0.00007500
H	0.30480700	1.50860000	0.00006900
O	1.23321500	-0.27650600	0.00001700

Acetonitrile

C	0.00000000	0.00000000	-1.17585100
H	1.02432500	0.00000000	-1.55388600
H	-0.51216300	0.88709200	-1.55388600
H	-0.51216300	-0.88709200	-1.55388600
C	0.00000000	0.00000000	0.28097900
N	0.00000000	0.00000000	1.43298400

2-Methylpridine

C	-1.86809400	-0.07094800	-0.00004800
C	-1.23448000	1.16685900	-0.00001100
C	0.15596400	1.20780000	0.00005300
C	0.87562200	0.00853800	0.00002300
C	-1.06980500	-1.21262900	0.00005000
H	-2.94822800	-0.15507100	-0.00014300
H	-1.81128000	2.08528400	-0.00003500
H	0.68121400	2.15601900	0.00010900
H	-1.52466300	-2.20001300	-0.00003500
N	0.26406000	-1.18577700	0.00002800
C	2.38226200	-0.01318500	-0.00004200
H	2.80418800	0.99342400	-0.00024900
H	2.75084500	-0.54876300	0.87886500
H	2.75069100	-0.54904600	-0.87885300

A-TS1

C	-1.41721400	-0.14056300	0.00000000
H	-1.38973600	-0.75110800	-0.90316000
H	-2.27347100	0.54070800	-0.00150600
H	-1.39127700	-0.74903700	0.90461200
C	0.56967500	0.55842000	-0.00002500
H	-0.31739500	1.19268800	0.00011900
O	1.30714000	-0.34254900	0.00001000

B-TS1

C	-1.43351000	-0.36245300	-0.10821600
H	-2.20846500	0.36280400	0.14925000
H	-1.70326600	-1.33026200	0.32737100
H	-1.40544100	-0.43773800	-1.19933900
C	-0.09964000	0.17311900	0.40505100
H	-0.06436800	0.12400600	1.51317600
O	0.37275100	1.28440100	-0.16723800
N	1.10160900	-0.78493100	-0.08892000
H	1.71928400	-1.13557000	0.64071400
H	1.31264400	0.30494900	-0.51630400
H	0.85523800	-1.53287400	-0.73553300

B-I1

C	-1.37800900	-0.35079300	-0.09531400
H	-2.10830000	0.37310400	0.27384000
H	-1.65157700	-1.34331800	0.27169700
H	-1.42227800	-0.35205900	-1.18838400
C	0.02872700	0.02215900	0.35967300
H	0.07091800	0.01176300	1.45967900
O	0.27659000	1.32904300	-0.13293200
N	1.09806100	-0.85818300	-0.09717000
H	1.11793900	-1.72238300	0.43404900
H	1.22239600	1.47508400	-0.01621300
H	0.96744500	-1.09544900	-1.07717000

B-I2

C	1.42419400	-0.40294300	-0.14743600
H	1.60231900	-1.34739600	0.36802700
H	2.32485400	0.21648600	-0.04968000
H	1.25146900	-0.57637500	-1.21019500
C	0.27814000	0.34841900	0.44899600
H	0.26687900	0.42414100	1.53725600
O	-1.20801600	-0.89609700	0.05290500
N	-0.40209500	1.21767100	-0.31227500
H	-1.07990300	0.23149100	-0.62911700
H	-1.09726900	-1.78047700	-0.32421200
H	-1.00356600	1.80435700	0.26125000

B-TS3

C	-1.23247400	-0.11516800	-0.00003400
H	-1.69569500	0.32091600	-0.88712900
H	-1.69543100	0.31785400	0.88870900

H	-1.36887400	-1.20062200	-0.00184400
C	0.22853700	0.14968600	0.00019700
H	0.23768300	1.70427200	-0.00036600
N	1.34394100	-0.33781600	-0.00008200
H	1.13835300	1.01517800	0.00022500

C-TS1

C	2.25230300	0.47755200	0.06875000
H	1.74448900	1.22404800	0.67545300
H	2.54446800	0.93128900	-0.88430600
H	3.17607600	0.17384500	0.57011300
C	1.40593100	-0.73041500	-0.17606400
H	1.89279000	-1.58409500	-0.65218300
N	0.18337600	-0.87887100	0.13647100
H	-0.74160700	-1.51723900	-0.23511200
C	-0.97067500	1.45333200	-0.20591800
H	-0.24986000	2.10461700	0.29700700
H	-1.95662500	1.91841700	-0.13446200
H	-0.72251200	1.36395000	-1.26617300
C	-1.08488100	0.06676600	0.42038800
H	-1.14549400	0.13663300	1.52440100
O	-1.93017800	-0.77534700	-0.18662200

C-I1

C	2.25290100	0.30883800	0.51418900
H	1.65147900	0.73741900	1.31472100
H	2.79632400	1.12134200	0.01944600
H	3.00858000	-0.34972100	0.95381000
C	1.45157700	-0.45286700	-0.51061900
H	2.05765000	-0.95606500	-1.27091300
N	0.19746100	-0.58890900	-0.63298500
H	-1.92690500	-1.35826300	-0.37026200
C	-1.27032400	1.32687100	-0.29640200
H	-0.47946900	2.08160300	-0.33523400
H	-2.09016800	1.70126700	0.31958300
H	-1.63975600	1.16092400	-1.31170400
C	-0.75564200	0.00969500	0.28795900
H	-0.34757900	0.18038600	1.29042500
O	-1.81043200	-0.91897000	0.48128300

C-TS2

C	2.41140600	0.27054500	0.48241500
H	3.06432400	0.93997000	-0.08828900
H	3.06698600	-0.41134000	1.03348100

H	1.84148000	0.87131400	1.19084500
C	1.54356300	-0.50854800	-0.46554800
H	2.07733200	-1.15559500	-1.16581100
N	0.27808200	-0.49670900	-0.57927500
H	-2.03189400	-1.59940700	-0.21038700
C	-1.36759700	1.28411700	-0.32661000
H	-1.59217500	2.13493200	0.30814600
H	-2.26074600	0.24650400	-0.12681700
H	-1.19879500	1.50132900	-1.37691700
C	-0.54956400	0.25773600	0.24473500
H	-0.36657200	0.24313100	1.31507000
O	-2.09667000	-0.88962300	0.44570800

C-I2

C	1.60491000	0.82284900	0.18664300
H	0.83466000	1.40003400	0.69663300
H	1.93340400	1.38139100	-0.69669700
H	2.48079500	0.72260900	0.83590500
C	1.12321300	-0.54402300	-0.21791500
H	1.88787600	-1.20317900	-0.63925100
N	-0.03986100	-1.04403100	-0.11844400
C	-1.77175900	0.67011100	-0.25508100
H	-2.69880100	1.06614300	0.13923100
H	-1.39780400	1.09026300	-1.18176500
C	-1.15256400	-0.34260900	0.35688200
H	-1.58390700	-0.78701000	1.25188300

C-TS3

C	-3.01463600	1.04058000	0.04788600
H	-2.11697700	1.65881500	0.04954900
H	-3.57899500	1.21750200	0.96900500
H	-3.66178300	1.34314500	-0.78195900
C	-2.68614100	-0.41787600	-0.07458800
H	-3.52147800	-1.12029900	-0.05701700
N	-1.53133400	-0.90798500	-0.19784700
C	0.67439800	-0.56431200	0.77521100
H	1.36814900	-1.49869700	0.37762800
H	0.29983100	-0.59863700	1.79889000
C	-0.26439300	-0.55877400	-0.27222700
H	0.16009300	-0.44884000	-1.27464300
C	2.04136000	1.52539200	-0.18510200
H	3.07157800	1.80757700	-0.41470900
H	1.63184000	2.25898800	0.51893200
H	1.47420600	1.57560900	-1.12040900

C	2.05653700	0.09888900	0.37928400
H	2.60000000	0.13042900	1.34744200
O	2.51876500	-0.83913600	-0.50632100

C-I3

C	-2.59732000	1.21308100	-0.33949100
H	-1.60203100	1.47575300	-0.69557100
H	-2.85409800	1.86815300	0.50030100
H	-3.33221700	1.41197000	-1.12631600
C	-2.69264000	-0.22854100	0.08109000
H	-3.69690900	-0.57274800	0.34515500
N	-1.77557400	-1.10414500	0.15053400
C	0.40361600	-0.11723300	0.64207700
H	2.19394600	-1.79915500	-0.28442300
H	0.01859900	0.40431300	1.51549000
C	-0.42545600	-0.84194700	-0.11563300
H	-0.03187300	-1.40068100	-0.96105100
C	2.29351900	1.39951400	-0.06327700
H	3.37831500	1.45997500	-0.17536000
H	1.97162500	2.15618100	0.65654100
H	1.82868400	1.61422700	-1.02843200
C	1.89104300	0.00010300	0.40051000
H	2.40761100	-0.20245100	1.35293400
O	2.36384900	-0.90454800	-0.59808200

C-TS4

C	-2.16759600	1.37246300	0.30373600
H	-1.11426800	1.49764900	0.04604300
H	-2.33461500	1.75101100	1.31758700
H	-2.78190400	1.99159500	-0.35998900
C	-2.63579800	-0.05361000	0.21487200
H	-3.66614300	-0.24407600	0.52457500
N	-1.98594500	-1.06327400	-0.20641600
C	0.37758800	-0.80371300	0.26439900
H	1.77757500	2.29696400	-1.08245600
H	0.18544500	-0.65623400	1.32249900
C	-0.66282800	-1.00110400	-0.57920000
H	-0.47953400	-1.17751700	-1.63786100
C	2.82198600	-0.37255300	0.65494300
H	2.73063100	0.82198800	0.38533000
H	3.79501600	-0.70173700	0.29593100
H	2.66075400	-0.54475200	1.71752300
C	1.71270100	-0.66183000	-0.20114600
H	1.89675100	-0.83891800	-1.25396800

O	1.81944800	1.54612800	-0.47199100

C-I4

C	-2.19872000	1.25670100	-0.32383000
H	-1.28961700	1.39399400	-0.90831500
H	-2.22148400	2.01223100	0.46933500
H	-3.07343100	1.44156300	-0.95563300
C	-2.29369900	-0.12171600	0.27098300
H	-3.24429100	-0.35920000	0.75652700
N	-1.43108100	-1.05531500	0.26385900
C	0.83139100	-0.13122400	0.22123100
H	0.60341900	0.56065500	1.02855300
C	-0.14283900	-0.93484400	-0.24882900
H	0.09041300	-1.67603700	-1.01139500
C	3.19275600	0.60579600	0.18744000
H	4.19345800	0.53784800	-0.22118300
H	3.03397400	1.33113400	0.97919900
C	2.19761400	-0.16958000	-0.26186200
H	2.40611400	-0.88578200	-1.05489700

C-TS5

C	1.84020000	-0.32243400	-0.01964400
C	1.45751200	0.99320200	-0.26579100
C	0.30412000	1.58744200	0.25476900
C	-1.09292200	-0.15406300	0.35263400
C	0.89105600	-1.36365400	0.09174800
H	2.83651800	-0.64043800	-0.31118700
H	2.02491200	1.53800700	-1.02107000
H	-0.06542100	2.49621200	-0.21450100
H	1.26634700	-2.37992100	-0.01602700
N	-0.41141400	-1.22728100	-0.03890000
C	-2.40786300	0.14382100	-0.31989500
H	-2.31350000	0.06399200	-1.40359900
H	-3.16542300	-0.57772900	0.00836200
H	-2.76117700	1.14458700	-0.06386400
H	-1.05000900	0.07782300	1.41020000
H	0.15503000	1.56255000	1.32106400

C-I5

C	-1.64777600	-0.07281900	0.45084900
C	-1.13139700	1.13739700	0.21521200
C	0.13477000	1.25197200	-0.58911000
C	1.00343600	-0.01865800	-0.47034400
C	-0.95283500	-1.26074900	-0.07080700

H	-2.58027900	-0.20721400	0.98813000
H	-1.63290300	2.03980300	0.55101400
H	0.71641300	2.12764700	-0.28304000
H	-1.49717800	-2.20737100	-0.06666800
N	0.23966800	-1.28177700	-0.52510900
C	1.85408500	-0.03976200	0.80902500
H	2.55546300	0.79962200	0.81813700
H	1.22480300	0.02498300	1.70054400
H	2.42362000	-0.96966300	0.86166200
H	1.68846100	-0.04412200	-1.32246100
H	-0.13776600	1.42447100	-1.64050300

C-TS6

C	1.84789700	-0.08053800	0.24766500
C	1.26289400	1.14748100	-0.08368400
C	-0.12021800	1.23853000	-0.23460400
C	-0.85555400	-0.04292800	0.13935400
C	1.07777200	-1.22172400	-0.09041700
H	2.91402100	-0.16684900	0.40769100
H	1.88497400	2.01974300	-0.25778400
H	-0.65396400	2.08993700	-0.63179600
H	1.59021700	-2.15100000	-0.33508000
N	-0.22311100	-1.22054000	-0.25953400
C	-2.36213600	-0.02581900	0.03016600
H	-2.79304500	0.85715000	0.50583900
H	-2.61614700	-0.01643200	-1.03281200
H	-2.78155700	-0.92725500	0.47573400
H	-0.70590400	-0.06934600	1.55065700
H	-0.38075300	0.81782900	1.08340900

Model of B acid site

Al	-0.26943900	0.00060800	-0.05237800
O	1.22416100	-0.00347100	0.83482900
O	-1.15896300	1.46221800	-0.10742400
O	-1.18293300	-1.44722400	-0.08373800
O	0.70568600	-0.02622900	-1.72728700
Si	2.44014600	-0.03718900	-1.77577700
H	0.23255200	-0.04730700	-2.56523100
Si	-2.10204800	-2.77899300	0.09642600
H	-1.59003000	-3.64990200	1.19028600
H	-3.51351500	-2.42786400	0.41503400
H	-2.10769000	-3.58091900	-1.16004700
Si	2.07476400	0.00839200	2.23629800

H	1.80691000	-1.20779600	3.05080100
H	3.52965400	0.04392700	1.92235800
H	1.75058000	1.20173700	3.06432000
Si	-2.04824400	2.81550300	0.06164800
H	-2.83890200	3.08227900	-1.17291000
H	-1.17887400	4.00076100	0.30395800
H	-2.99996900	2.70811800	1.20149300
H	2.70544300	-0.05366700	-3.23534600
H	2.94312700	-1.26950500	-1.15050800
H	2.95516800	1.20188800	-1.17467200

Model of L acid site

O	-1.45089200	-0.83512900	-0.62310300
O	1.44701000	-0.83739000	-0.62330200
O	-0.00060000	1.67184000	-0.62451500
Si	0.14119700	2.58445100	0.75781100
Si	2.17255300	-1.41222800	0.75754300
H	2.07967900	-0.42381200	1.86621100
H	1.53738200	-2.67681200	1.21073800
H	3.59886900	-1.65976100	0.43541800
Si	-2.30989500	-1.17043200	0.76022600
H	-1.40877700	-1.59970100	1.86401700
H	-3.07107700	0.01978600	1.22079800
H	-3.25234400	-2.26892400	0.43709600
H	-0.35881900	3.94439600	0.44127600
H	1.55634200	2.66538800	1.20402300
H	-0.66316000	2.00836400	1.86950200
Co	-0.00134100	-0.00105800	-1.01629100

Transition state for the formation of acetonitrile at B acid site

Al	-0.43790200	0.19508600	-0.02363900
O	-2.11588400	-0.19752100	-0.05660100
O	0.03824900	1.84564800	-0.09198500
O	0.37619200	-0.68819300	-1.39416800
O	0.30658200	-0.56930600	1.44544300
Si	-0.40508300	-1.28015500	2.78002400
Si	-0.25492500	-1.62626500	-2.62899800
H	-0.94216500	-2.82414900	-2.08946700
H	-1.19672500	-0.84108900	-3.46157700
H	0.89570200	-2.06140300	-3.46216100
Si	-3.74453400	-0.17217700	-0.10967400
H	-4.32381900	-0.79090900	1.11509300
H	-4.27434400	1.21646700	-0.21168800
H	-4.24620900	-0.93688900	-1.28549900

Si	0.23693800	3.45615500	-0.16937800
H	-0.16860400	4.12234500	1.10022800
H	-0.56001500	4.05905300	-1.27461000
H	1.66874900	3.79775400	-0.41402800
H	-1.34655000	-0.34129200	3.43677200
H	0.68945700	-1.62227500	3.72405900
H	-1.12498900	-2.52214500	2.40586300
C	4.77332600	-0.41770400	-0.44315600
H	4.85466700	0.49219400	-1.04020800
H	4.94506700	-1.27438400	-1.09670500
H	5.51280400	-0.40403300	0.36052700
C	3.42779800	-0.50040400	0.15204300
H	2.61754300	-0.51379200	-1.21805300
N	2.79688700	-0.54906600	1.14943300
H	1.67338300	-0.57290500	1.35189500
H	1.73916100	-0.57737900	-1.36164400

Transition state for the formation of 2-methylpyridine at B acid site

C	4.30823000	1.02605000	0.54746100
H	5.17330700	1.51496500	0.99136200
C	3.36925900	1.81130000	-0.18993800
H	3.42801100	2.89156300	-0.16230800
C	2.49462600	-0.32520100	-1.02265000
H	1.46800600	-0.72214200	-1.11848400
H	2.99909400	-0.67925000	-1.94180300
C	2.51245400	1.15518600	-1.01096900
H	1.85710800	1.68090700	-1.69305500
N	4.22727500	-0.27232400	0.73850600
C	3.18730400	-0.92426000	0.15302800
H	2.00443000	-0.46072600	1.28742400
C	3.09743700	-2.39719100	0.38355200
H	3.44300400	-2.64500300	1.38631800
H	2.08588100	-2.76471300	0.21665200
H	3.76656200	-2.89159100	-0.33228200
Al	-1.10725200	0.03117900	-0.06640800
O	-2.82040000	-0.07636500	0.14517500
O	-0.55238800	1.52656300	-0.80192100
O	-0.41650600	-1.30409900	-1.00529600
O	-0.32348700	-0.09325900	1.55979200
Si	-0.88523900	-0.07960700	3.12049900
H	1.19553800	-0.31905500	1.40655200
Si	-0.85877500	-2.61035300	-1.88646000
H	-1.58688200	-3.62603400	-1.07656400
H	-1.70880300	-2.25498200	-3.05617900

H	0.37682900	-3.26526100	-2.41364100
Si	-4.44083100	-0.17261700	0.18009200
H	-5.07765000	1.06513900	-0.35457000
H	-4.94006300	-1.31753000	-0.63486500
H	-4.94038200	-0.36457300	1.57154000
Si	-0.92317700	3.05326600	-1.22989200
H	0.29145400	3.69453400	-1.82595800
H	-1.33423700	3.89817000	-0.07259900
H	-2.00144200	3.12469700	-2.25468100
H	0.29674500	-0.12440400	4.02409600
H	-1.74020700	-1.25910600	3.41099200
H	-1.65426500	1.15766400	3.41157300

Transition state for the formation of acetonitrile at L acid site

H	-1.55741500	1.69053400	0.35696700
H	-1.60942800	0.03368400	-1.00482600
O	1.68698000	0.23896800	-0.45099300
O	-0.42791300	1.54397400	0.22764300
O	-0.55909200	-1.60369100	0.10336800
Si	0.13787100	-2.44238100	1.35869400
Si	0.78893400	2.47660600	0.97704800
H	1.48505800	1.71846300	2.03513300
H	1.71320600	3.04860800	-0.01994100
H	0.00797000	3.57377100	1.60507700
Si	3.14227300	-0.39729900	-0.86176800
H	4.03702400	0.67934500	-1.37038600
H	3.81490600	-1.04581900	0.29773900
H	3.01732000	-1.42704000	-1.93728700
H	-0.62917100	-3.70500200	1.51666400
H	0.06477400	-1.66207300	2.62309400
H	1.56158800	-2.78272600	1.09951000
Co	-0.11077300	-0.05030700	-0.56729600
C	-3.72523500	-0.71090300	-0.93591400
H	-3.26037000	-1.65814800	-0.65767400
H	-3.78243400	-0.66041500	-2.02513300
H	-4.72695000	-0.63826300	-0.50928400
C	-2.89406200	0.40007500	-0.41679800
N	-2.85661700	1.38676500	0.24969000

Transition state for the formation of 2-methylpyridine at L acid site

C	3.06411200	1.72810500	0.18745400
C	2.42134700	1.49227400	-0.98141900
C	2.02327100	0.12402000	-1.34077200
C	2.52370300	-0.93767800	-0.41128000

C	3.44174700	0.63395500	1.03206800
H	3.34841000	2.73529300	0.47085800
H	2.18835700	2.29917900	-1.66544500
H	2.15518400	-0.11105800	-2.40322700
H	3.97136000	0.83106500	1.96070800
N	3.24856200	-0.62023900	0.71912700
C	2.80318600	-2.31094200	-0.99610800
H	1.95940300	-2.67903600	-1.58731700
H	3.68027400	-2.28280800	-1.65442100
H	3.01086700	-3.02228700	-0.19553800
H	1.25283200	-1.15279800	0.17884300
H	0.81901900	0.12085300	-1.33133200
O	-2.56671600	-0.42108400	-0.89255100
O	0.09120000	-1.16974600	0.33255900
O	-0.51116200	1.64793800	-0.33414500
Si	-0.92996400	2.57719700	0.96014500
Si	-0.50813800	-1.97117400	1.70974500
H	-1.14527100	-0.98805200	2.61302800
H	-1.49084700	-2.98980600	1.28142100
H	0.66314600	-2.60408900	2.35517700
Si	-4.08600800	-0.40106900	-0.26941700
H	-4.11389700	-0.92910900	1.12693800
H	-4.65673600	0.97355600	-0.23872500
H	-4.97320200	-1.26195700	-1.09813600
H	-0.73088500	4.00158200	0.58421400
H	-0.09360200	2.28710900	2.16088000
H	-2.35067600	2.38433400	1.37009200
Co	-0.83951500	-0.03610800	-0.75389200

Acetic acid

C	-1.39368000	-0.11814700	-0.00001600
H	-1.67249600	-0.70287000	-0.87943200
H	-1.91956000	0.83367900	-0.00133000
H	-1.67272800	-0.70036800	0.88101000
O	0.78520500	-1.03878300	-0.00000700
H	1.72372900	-0.79865700	0.00011000
O	0.63387500	1.20225300	0.00000700
C	0.09174900	0.12822200	-0.00004500

D-TS1

C	-1.28677700	0.66128600	0.57434100
H	-0.80494800	1.29566000	1.31856400
H	-2.04356500	0.03621000	1.05981700
H	-1.78890500	1.28911200	-0.16171300

O	1.09134400	1.01493500	-0.56716000
H	0.82722700	1.93567100	-0.47012800
O	-0.56537100	-0.96174400	-1.07311000
C	-0.30932200	-0.23131800	-0.15859700
N	0.85083000	-0.75249800	0.85981700
H	0.60413600	-0.78933800	1.84409400
H	1.43021400	0.14491400	0.49379600
H	1.18884100	-1.65008000	0.52454600

D-I1

C	-1.36137700	-0.34688600	-0.00019000
H	-1.46081200	-1.42881900	-0.10829000
H	-1.89716000	0.14637600	-0.81253700
H	-1.83171700	-0.03906300	0.93631200
O	0.35385600	1.33170400	0.00068000
C	0.07730600	0.14816900	-0.00328500
N	1.03523600	-0.82707700	-0.00352900
H	2.00191400	-0.54312500	0.01593400
H	0.81470100	-1.80716300	0.00869600

D-TS2

C	1.46100600	0.09378500	-0.00000700
H	1.85333700	-0.42164600	-0.87928400
H	1.85321200	-0.42068500	0.87989000
H	1.80618100	1.12714600	-0.00053600
O	-0.65262600	-1.13501200	-0.00000100
C	-0.02908600	-0.00726800	-0.00000200
N	-0.93429600	0.93673900	0.00000200
H	-0.74404500	1.93103200	-0.00000600
H	-1.59912300	-0.21202600	-0.00001300

D-I2

C	1.39984800	-0.06537700	-0.00001600
H	1.90030800	0.90237400	-0.00016900
H	1.71123600	-0.63378000	-0.87989100
H	1.71115000	-0.63336600	0.88019800
O	-0.71232800	-1.11430000	0.00000000
C	-0.09562500	0.09418300	-0.00000500
N	-0.79618100	1.14994100	0.00000100
H	-0.21393700	1.98317800	-0.00001600
H	-1.66220700	-0.92643200	-0.00000100

D-TS3

C	-1.49071400	-0.33662100	-0.00396000

H	-1.60903700	-0.96921700	0.87766000
H	-1.56406300	-0.96588300	-0.89158300
H	-2.28129100	0.41690100	-0.01713700
C	-0.18886300	0.34679700	0.01777400
N	0.49325000	1.33571500	0.01909900
H	1.39906700	0.42801300	-0.03345700
O	1.16768500	-0.87073400	-0.10806600
H	1.33856100	-1.35500100	0.71246400

Acetone

C	1.29145800	-0.61343500	-0.00153000
H	1.30313800	-1.33167800	-0.82705100
H	1.37484100	-1.19120700	0.92492400
H	2.14149200	0.06221200	-0.08499200
C	-0.00000200	0.18640600	0.00000000
O	-0.00000300	1.39552100	0.00000000
C	-1.29145300	-0.61343700	0.00153000
H	-1.37482900	-1.19121500	-0.92492200
H	-1.30313700	-1.33167800	0.82705500
H	-2.14150000	0.06219300	0.08498300

E-TS1

C	-0.86514400	1.27872300	-0.25475900
H	-1.75391900	1.34398800	0.37693900
H	-1.18006500	1.30534100	-1.30288500
H	-0.24400700	2.14944000	-0.03079500
C	-0.11018400	-0.00000700	0.12645700
O	0.44277400	0.00003200	1.34954600
N	1.31983000	-0.00027600	-0.66778100
H	1.53924500	-0.83587700	-1.20631500
H	1.54354500	-0.00031000	0.50118700
H	1.53939500	0.83542200	-1.20609200
C	-0.86558500	-1.27847800	-0.25462900
H	-1.75461200	-1.34315000	0.37681100
H	-1.18019600	-1.30516700	-1.30287200
H	-0.24491200	-2.14944500	-0.03028900

E-I1

C	-1.26332600	-0.80291500	-0.29354300
H	-1.33842300	-1.66655700	0.37152500
H	-1.25386700	-1.15633800	-1.32771600
H	-2.14828000	-0.18031300	-0.14032400
C	-0.00250000	0.01162100	0.01234600
O	-0.14398900	0.42240900	1.37119100

N	0.13546200	1.22931400	-0.79219200
H	0.40113300	1.01138800	-1.74746900
H	0.51960600	1.10983300	1.50442700
H	-0.75290300	1.72194600	-0.82549700
C	1.26865800	-0.82851200	-0.16206100
H	1.24596700	-1.67828700	0.52178400
H	1.36550400	-1.20741400	-1.18435400
H	2.14794800	-0.21988900	0.06298600

E-TS2

C	0.28779000	1.52305300	0.06849100
H	0.33340900	1.84012900	-0.97308800
H	1.15961600	1.93791000	0.59318400
H	-0.61073500	1.91670100	0.53979000
C	0.33189300	0.02982100	0.19342000
O	-1.53431900	-0.33989400	-0.69002300
N	-0.29805500	-0.51752000	1.23939500
H	-1.32919400	-0.40199000	0.68788500
H	-2.12965000	0.21621400	-1.21012300
H	-0.09680600	-1.51189800	1.31464700
C	1.38766300	-0.71240400	-0.57019700
H	2.32549100	-0.68995100	-0.00110600
H	1.09155700	-1.75163900	-0.71457000
H	1.57316600	-0.25650100	-1.54248000

E-I2

C	1.34982800	-0.50626000	-0.00002600
H	1.46598300	-1.14877900	-0.87942000
H	1.46620200	-1.14783300	0.88005500
H	2.13324100	0.24998100	-0.00041600
C	-0.00402100	0.16162000	-0.00008000
N	-0.05892400	1.43257900	0.00004800
H	-1.03210600	1.74922800	-0.00022500
C	-1.19956600	-0.76814600	-0.00003900
H	-2.13901900	-0.21155000	-0.00089700
H	-1.17921300	-1.42208700	-0.87810500
H	-1.18006700	-1.42029100	0.87953900

E-TS3

C	-1.19262500	-0.90157200	-0.00004300
H	-1.00751900	-1.50859500	0.88758200
H	-1.00577000	-1.50950900	-0.88665400
H	-2.23093900	-0.55963800	-0.00120100
C	-0.33428600	0.31639400	0.00020500

N	-0.35688400	1.53351400	-0.00005000
H	0.81471300	0.86954900	-0.00019900
C	1.57307400	-0.44766000	0.00001000
H	1.62242100	-1.05218100	-0.90426900
H	2.40454000	0.27324900	-0.00132100
H	1.62376200	-1.05044800	0.90538300

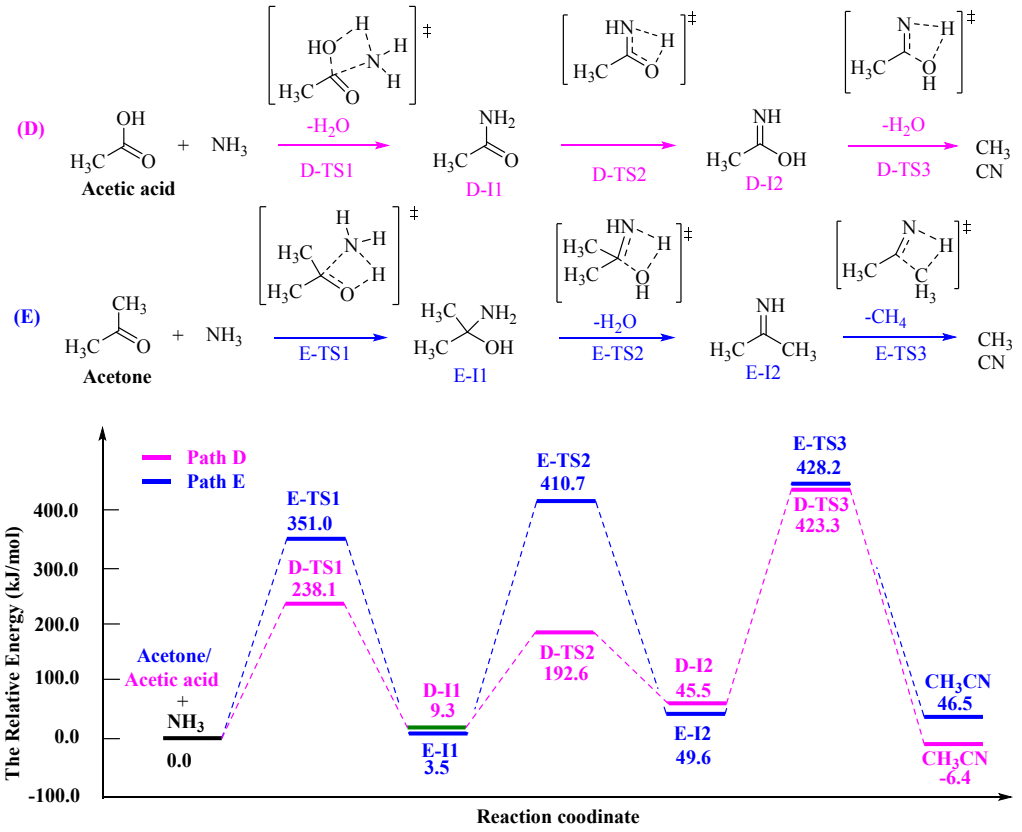

Fig. S9 Evolution pathways and energy diagrams for acetonitrile formation from acetic acid and acetone