Supplementary Materials

Selective Production of Terephthalonitrile and Benzonitrile via Pyrolysis of Polyethylene Terephthalate (PET) with Ammonia over Ca(OH)2/Al2O3 Catalysts

Lujiang Xu[1, 2], Xin-wen Na[1], Le-yao Zhang[1], Qian Dong[1], Guo-hua Dong[1], Yi-tong Wang[3], and Zhen Fang [1,*]

1 Biomass Group, College of Engineering, Nanjing Agricultural University, 40 Dianjiangtai Road, Nanjing, Jiangsu 210031, China

2 Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Southeast University, Nanjing, 210096, China.

3 College of Metallurgy and Energy, North China University of Science and Technology, 21 Bohai Street, Tangshan, 063210, China.

* Correspondence: zhenfang@njau.edu.cn

Table of Contents:

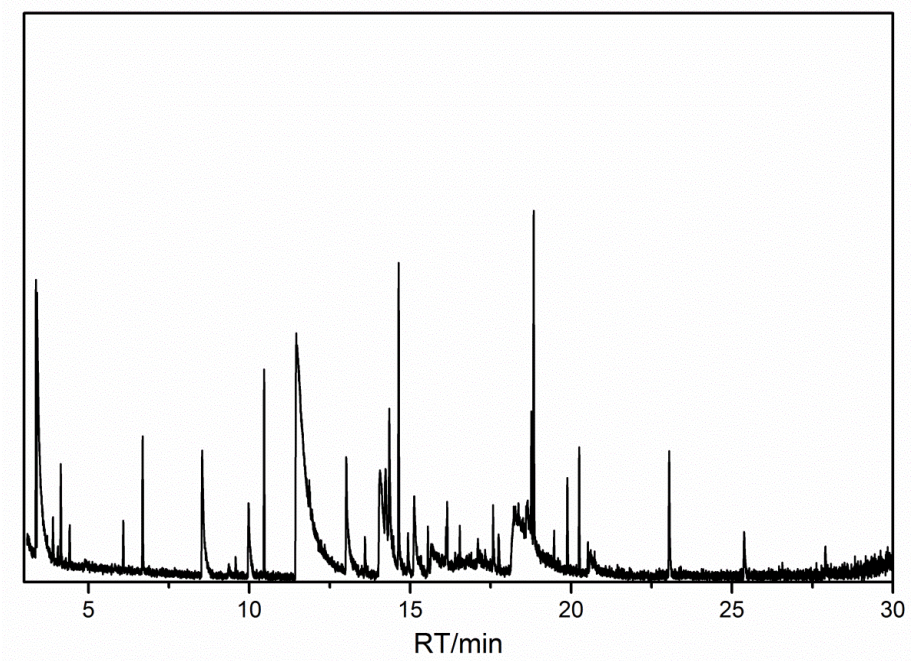


Figure S1. The Chemical compositions of pyrolysis PET with ammonia at 650 ºC

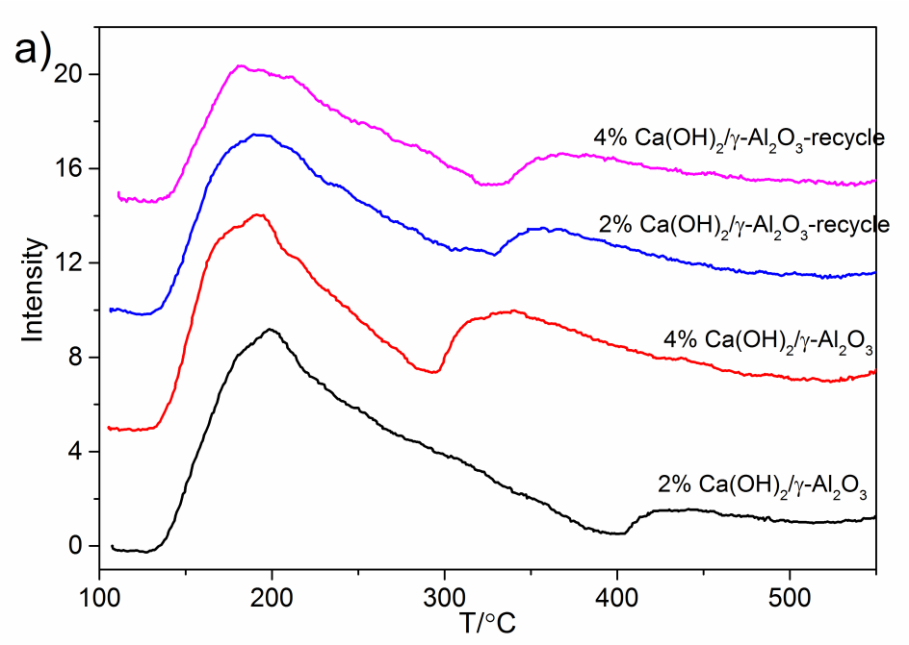


Figure S2. The NH_3-TPD spectra of fresh and used $Ca(OH)_2/\gamma Al_2O_3$ catalysts

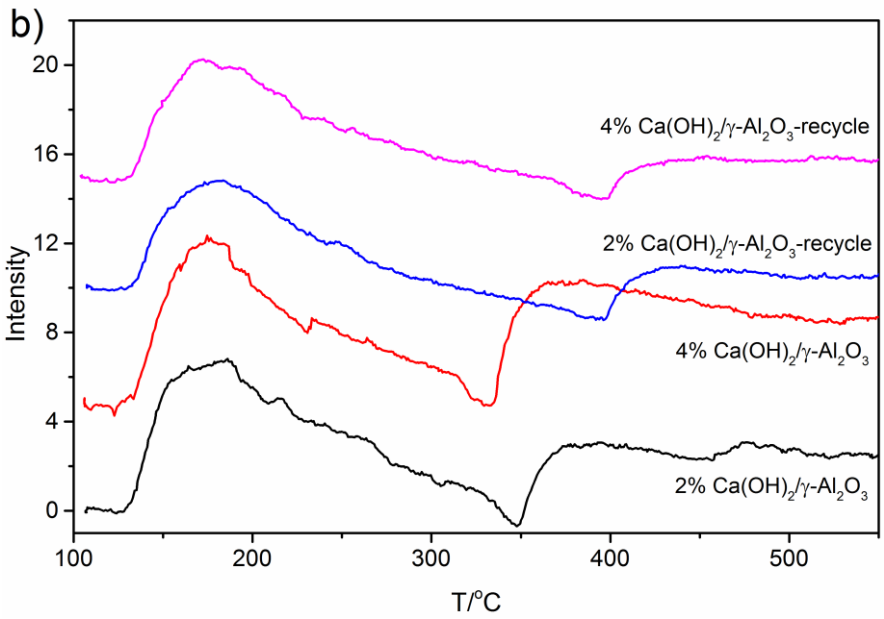


Figure S3. CO_2-TPD curves of fresh and used $Ca(OH)_2/\gamma Al_2O_3$ catalysts

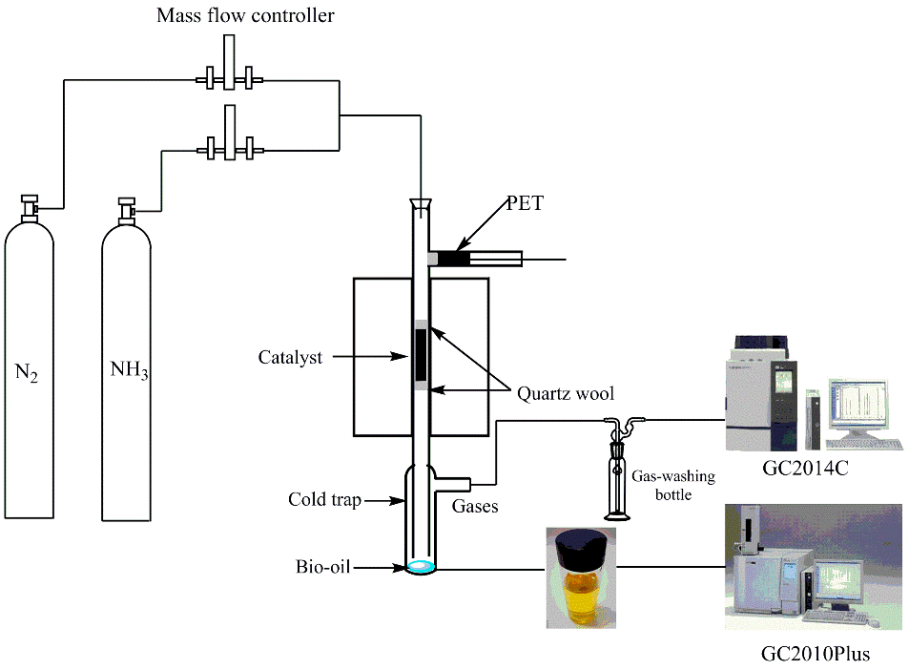


Figure S4 The schematic diagram of the pyrolysis system.

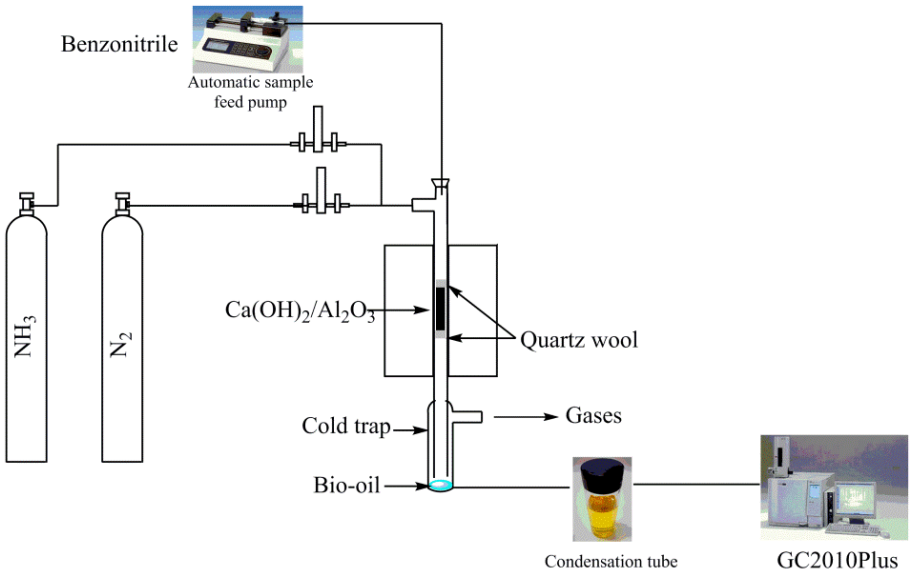


Figure S5 The schematic diagram of the liquid injection pyrolysis system

Table S1. The detailed chemical compositions of pyrolysis PET with ammonia at 650 ºC

No.	RT/min	Chemicals	Peak area (%)	M.W.
1	3.37	Butanoic acid, methyl ester	1.89	102.068
2	3.40	1-Butanol, 3-methoxy-	2.10	104.084
3	3.90	Ethylene glycol diglycidyl ether	0.94	174.089
4	4.05	1-Pentanamine	0.27	87.105
5	4.14	Toluene	1.80	92.063
6	4.42	Butanoic acid, 2-methyl-, methyl ester	0.77	116.084
7	6.08	p-Xylene	0.85	106.078
8	6.68	Styrene	2.62	104.063
9	8.53	Benzonitrile	5.71	103.042
10	9.97	Acetophenone	0.99	120.06
11	10.46	Dodecane	3.45	170.203
12	11.46	Benzoic acid	27.87	122.037
13	13.01	terephthalonitrile	3.72	128.037
14	14.04	Benzamide	9.08	121.053
15	14.35	Benzoic acid, 4-cyano-, methyl ester	5.60	161.048
16	14.64	Biphenyl	5.62	154.078
17	15.13	Butyl benzoate	3.99	206.131
18	15.55	Benzene, 1,2,4-triethyl-	0.71	162.141
19	16.15	1,4-Benzenedicarboxylic acid, dimethyl ester	1.07	194.058
20	16.54	Benzoic acid, 4-acetyl-, methyl ester	0.60	178.06
21	17.10	4-Cyanobenzoic acid, isopropyl ester	0.46	189.08
22	17.57	Phenol, 3-(2-phenylethenyl)-, (E)-	0.99	196.089
23	17.74	Benzophenone	0.60	182.07
24	18.16	Benzoic acid, 4-cyano-, methyl ester	0.20	161.048
25	18.61	4-Cyanobenzoic acid, butyl ester	0.48	203.1
26	18.76	9-Acridinamine	1.97	194.084
27	18.84	p-Phenylbenzonitrile	5.44	179.073
28	19.47	Anthracene	0.62	178.078
29	19.88	Ethanone, 1-[1,1'-biphenyl]-3-yl-	1.92	196.089
30	20.25	Phthalic acid, heptyl trans-hex-3-enyl ester	2.31	346.214
31	20.53	4-Phenylbenzhydrazide	0.57	212.1
32	23.05	Benzoic acid, 3-ethylphenyl ester	3.30	226.099
33	25.37	Benzaldehyde, 4-cyano-, benzoylhydrazone	0.49	249.09

Table S2. C-C Bond dissociation energy of some model compounds @25 ºC

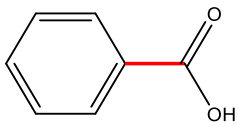
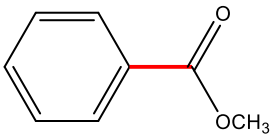
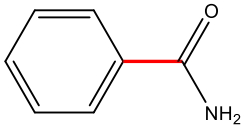
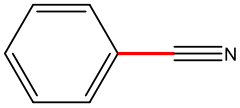
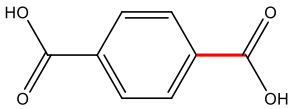
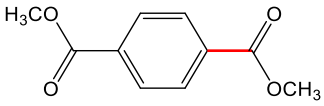
Entry	Feedstock	Chemical Structure	Bond dissociation energy (kcal/mol) @ 25 ºC	Bond dissociation energy (kcal/mol) @ 650 ºC
1	Benzoic acid		87.12	58.95
2	Methyl benzoate		85.41	56.65
3	Benzamide		77.20	49.05
4	benzonitrile		120.55	95.67
5	Terephthalic acid		86.27	58.22
6	Dimethyl terephthalate		84.97	56.35

Table S3. Elemental analyses (%) of PET plastic

C	**H**	**S**	**N**	**O**
62.34	4.36	0	0.04	33.26

Table S4. Integration parameters and their values set in mass spectrometry detector (MSD) chemstation.

Integrator Event Name	**Value**	**Time**
Initial Area Reject	0.5% of largest peak	Initial
Initial Peak Width	0.075	Initial
Shoulder Detection	OFF	Initial
Initial Threshold	17.5	Initial
Threshod	19.0	0.001