

Supplementary Material

Efficient pyrolysis of low-density polyethylene for regulatable oil and gas products by ZSM-5, HY and MCM-41 catalysts

Ting Liu¹, Yincui Li¹, Yifan Zhou², Shengnan Deng¹, Huawei Zhang^{1*}

¹ School of Environmental and Municipal Engineering, Qingdao University of Technology, Qingdao 266033, China

² College of Chemical and Biological Engineering, Shandong University of Science and Technology, Qingdao 266590, China

* Correspondence: sdkdzhw@163.com; Tel.: +86-0532-85071133

2. Materials and methods

2.3 Characterization

The N₂ adsorption-desorption isotherm of the adsorbent was measured at 77 K using the ASAP 2020 volume adsorption analyzer. The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area. The pore size distribution map is calculated by the Barrett-Joyner-Halenda (BJH) method. The morphology and structure of ZSM-5, HY and MCM-41 were examined by scanning electron microscope (SEM, JEOL, JSM-6700F, Japan) and transmission electron microscope (HRTEM, JEOL, JEM-2100F, Japan). The acidity values for the various catalysts were determined by NH₃-TPD (ChemiSorb 2920, Micromeritics Instrument Corporation, USA), the experimental samples were first heated to 500 °C in a helium atmosphere of 50 cm³/min and stayed for 1 h. Then the temperature was lowered to 100 °C, and the ammonia was absorbed for 90 min to saturation at the ammonia flow rate of 35 cm³/min. The samples were then purged at the same temperature for 120 min under continuous helium flow. Finally, the samples were heated to 600 °C in helium atmosphere at a heating rate of 10 °C/min. The desorbed ammonia gas in this process was detected by mass spectrometry.

3. Results and discussion

Tables:

Table S1. Liquid product composition of LDPE at different temperatures.

Table S2. Liquid product composition of LDPE at different temperatures.

Table S3. Liquid phase GC-MS table of catalytic pyrolysis of LDPE by ZSM-5 molecular sieve at 500 °C.

Table S4. Liquid phase GC-MS table of catalytic pyrolysis of LDPE by HY molecular sieve at 500 °C.

Table S5. Liquid phase GC-MS table of catalytic pyrolysis of LDPE by MCM-41 molecular sieve at 500 °C.

Table S1. Liquid phase products of LDPE pyrolysis at different temperatures.

component	respective percentages (%)			
	500 ° C	550 ° C	600 ° C	650 ° C
C ₇ H ₈	0.13	0.16	0.19	0.49
C ₈ H ₁₆	0.03	0.09	0.50	1.20
C ₈ H ₁₈	0.04	0.12	0.32	0.50
C ₈ H ₁₀	0.04	0.15	0.20	0.25
C ₉ H ₁₈	0.06	0.10	0.41	0.90
C ₉ H ₂₀	0.07	0.23	0.56	1.20
C ₁₀ H ₂₀	0.11	0.98	1.00	1.57
C ₁₀ H ₂₂	0.16	0.12	1.16	1.30
C ₁₁ H ₂₂	0.93	0.53	1.29	1.75
C ₁₁ H ₂₄	0.50	0.77	1.64	1.99
C ₁₂ H ₂₂	0.37	1.11	0.28	0.35
C ₁₂ H ₂₄	0.58	0.18	1.49	1.89
C ₁₂ H ₂₆	1.19	1.06	1.91	1.86
C ₁₃ H ₂₄	0.35	1.49	0.32	0.44
C ₁₃ H ₂₆	1.72	0.23	2.06	2.44
C ₁₃ H ₂₈	2.33	1.43	1.89	1.99
C ₁₄ H ₂₆	0.47	1.88	0.39	0.53
C ₁₄ H ₂₈	2.17	2.36	2.53	2.94
C ₁₄ H ₃₀	1.18	2.42	1.97	2.08
C ₁₅ H ₂₈	0.44	1.93	0.41	0.53
C ₁₅ H ₃₀	2.01	0.33	2.44	3.37
C ₁₅ H ₃₂	2.39	2.18	2.26	2.27
C ₁₆ H ₃₀	0.57	0.55	0.50	0.55
C ₁₆ H ₃₂	2.64	0.43	2.36	2.76
C ₁₆ H ₃₄	2.26	2.54	2.29	2.24
C ₁₇ H ₃₂	0.48	2.43	0.41	0.49
C ₁₇ H ₃₄	2.36	0.36	2.47	2.56
C ₁₇ H ₃₆	2.05	2.47	2.19	2.11
C ₁₈ H ₃₄	0.49	2.38	0.46	0.53
C ₁₈ H ₃₆	2.32	2.46	2.38	2.47
C ₁₈ H ₃₈	1.79	2.47	2.17	1.99
C ₁₉ H ₃₆	0.34	2.39	0.37	0.42
C ₁₉ H ₃₈	3.15	0.47	2.78	3.23
C ₁₉ H ₄₀	2.69	2.70	2.22	1.96
C ₂₀ H ₃₈	0.42	2.95	0.40	0.45
C ₂₀ H ₄₀	2.77	0.49	2.39	2.81
C ₂₀ H ₄₂	3.04	2.72	2.29	1.93
C ₂₁ H ₄₀	0.32	0.67	0.46	0.41
C ₂₁ H ₄₂	2.99	2.50	2.46	2.71
C ₂₁ H ₄₄	2.91	2.76	2.39	2.16
C ₂₂ H ₄₂	0.53	2.82	0.72	0.81
C ₂₂ H ₄₄	2.80	2.58	3.34	3.52

C ₂₂ H ₄₆	4.55	2.65	2.90	1.96
C ₂₃ H ₄₄	2.36	3.39	0.73	0.41
C ₂₃ H ₄₆	3.57	0.63	2.30	2.16
C ₂₃ H ₄₈	3.46	2.57	2.65	1.95
C ₂₄ H ₄₈	2.33	2.40	2.75	2.89
C ₂₄ H ₅₀	3.03	3.02	2.60	1.70
C ₂₅ H ₅₀	3.36	3.00	1.88	1.49
C ₂₅ H ₅₂	3.12	2.37	2.08	1.51
C ₂₆ H ₅₂	1.95	2.80	2.25	2.12
C ₂₆ H ₅₄	2.59	1.90	2.53	1.85
C ₂₇ H ₅₄	2.01	2.28	2.12	1.59
C ₂₇ H ₅₆	3.24	2.04	2.52	2.34
C ₂₈ H ₅₆	2.82	2.71	2.01	1.51
C ₂₈ H ₅₈	1.24	1.90	2.96	2.19
C ₂₉ H ₆₀	2.76	3.15	3.44	3.29
C ₃₀ H ₆₂	2.02	2.52	2.87	1.89
others	1.40	1.68	1.14	1.20
Total	100.00	100.00	100.00	100.00

Table S2. Liquid product composition of LDPE at different temperatures.

component	respective percentages (%)			
	500 ° C	550 ° C	600 ° C	650 ° C
α -Alkene	4.46	5.02	5.46	3.12
Alkene	39.49	45.53	49.46	52.78
Alkane	54.48	57.46	43.55	42.16
Aromatics	0.17	0.31	0.39	0.74
Others	1.40	1.68	1.14	1.20
Total	100.00	100.00	100.00	100.00

Table S3. Liquid phase GC-MS table of catalytic pyrolysis of LDPE by ZSM-5 molecular sieve at 500 °C.

component	chemical formula	respective percentages (%)
n-Heptane	C ₇ H ₁₆	0.23
2-Methyl hexane	C ₇ H ₁₆	0.07
3-Methyl hexane	C ₇ H ₁₆	0.23
2,3-Dimethyl pentane	C ₇ H ₁₆	0.06
3-Heptene	C ₇ H ₁₄	0.05
3-Methyl 1-hexene	C ₇ H ₁₄	0.63
4-Methyl 1-hexene	C ₇ H ₁₄	0.19
3-Ethyl pentene	C ₇ H ₁₄	0.12
n-Octane	C ₈ H ₁₈	0.12
2-Methyl heptane	C ₈ H ₁₈	0.10
3-Methyl heptane	C ₈ H ₁₈	0.11
4-Methyl heptane	C ₈ H ₁₈	0.37
3-Ethyl hexane	C ₈ H ₁₈	0.16
2,3-Dimethyl hexane	C ₈ H ₁₈	0.23
2,4-Dimethyl hexane	C ₈ H ₁₈	0.07
2,5-Dimethyl hexane	C ₈ H ₁₈	0.11
3,4-Dimethyl hexane	C ₈ H ₁₈	0.05
3-Ethyl 2-methyl pentane	C ₈ H ₁₈	0.05
2,3,4-Trimethyl pentane	C ₈ H ₁₈	0.02
4-Octene	C ₈ H ₁₆	2.37
n-Nonane	C ₉ H ₂₀	1.03
2-Methyl octane	C ₉ H ₂₀	0.24
3-Methyl octane	C ₉ H ₂₀	1.83
4-Methyl octane	C ₉ H ₂₀	1.86
3-Ethyl heptane	C ₉ H ₂₀	3.51

2,2-Dimethyl heptane	C ₉ H ₂₀	0.88
2,6-Dimethyl heptane	C ₉ H ₂₀	0.51
2,3,5-Trimethyl hexane	C ₉ H ₂₀	0.57
3-Ethyl 2,4-dimethyl pentane	C ₉ H ₂₀	2.05
1-Nonene	C ₉ H ₁₈	0.02
n-Decane	C ₁₀ H ₂₂	0.27
3-Methyl nonane	C ₁₀ H ₂₂	1.27
2,2-Dimethyl octane	C ₁₀ H ₂₂	0.44
2,3-Dimethyl octane	C ₁₀ H ₂₂	0.53
2,5-Dimethyl octane	C ₁₀ H ₂₂	0.74
2,6-Dimethyl octane	C ₁₀ H ₂₂	0.13
2,7-Dimethyl octane	C ₁₀ H ₂₂	0.46
1-Decene	C ₁₀ H ₂₂	1.04
Limonene	C ₁₀ H ₁₆	1.65
5-Undecene, (E)-	C ₁₁ H ₂₂	0.24
n-Undecane	C ₁₁ H ₂₄	1.51
6-Ethyl 2-methyl octane	C ₁₁ H ₂₄	1.24
Toluene	C ₇ H ₈	11.56
Ethylbenzene	C ₈ H ₁₀	3.24
(m,p)-Xylene	C ₈ H ₁₀	7.37
o-Xylene	C ₈ H ₁₀	3.27
Propylbenzene	C ₉ H ₁₂	0.24
1-Ethyl 2-methyl benzene	C ₉ H ₁₂	1.72
1-Ethyl 3-methyl benzene	C ₉ H ₁₂	0.24
1,2,3-Trimethyl benzene	C ₉ H ₁₂	1.98
Cumene	C ₉ H ₁₂	0.74
1,2,4-Trimethyl benzene	C ₉ H ₁₂	0.37
1,3,5-Trimethyl benzene	C ₉ H ₁₂	1.79
2-Ethyl 1,4-dimethyl benzene	C ₁₀ H ₁₄	0.94

2-Ethyl 3,5-dimethyl benzene	C ₁₀ H ₁₄	0.83
4-Ethyl 1,2-dimethyl benzene	C ₁₀ H ₁₄	0.72
1,2,3,5-Tetramethyl benzene	C ₁₀ H ₁₄	0.53
1,2,4,5-Tetramethyl benzene	C ₁₀ H ₁₄	0.83
2-Methyl 2-propenyl benzene	C ₁₀ H ₁₂	0.41
<hr/>		
Naphthalene	C ₁₀ H ₈	1.26
1H-Indene, 1,1-dimethyl-	C ₁₁ H ₁₂	0.24
1,3-Diethyl 5-methyl benzene	C ₁₁ H ₁₆	0.48
1,1-Dimethyl propylbenzene	C ₁₁ H ₁₆	0.56
Azulene	C ₁₀ H ₈	2.36
1-Methyl naphthalene	C ₁₁ H ₁₀	8.60
2-Methyl naphthalene	C ₁₁ H ₁₀	0.38
Naphthalene, 2-ethyl-	C ₁₂ H ₁₂	12.88
Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl-	C ₁₂ H ₁₆	0.35
Naphthalene, 1,4,6-trimethyl-	C ₁₃ H ₁₄	0.75
Naphthalene, 1,4,6-trimethyl-	C ₁₃ H ₁₄	0.13
Naphthalene, 1,6,7-trimethyl-	C ₁₃ H ₁₄	0.16
Naphthalene, 1,4,6-trimethyl-	C ₁₃ H ₁₄	0.25
Naphthalene, 2,3,6-trimethyl-	C ₁₃ H ₁₄	0.25
Naphthalene, 1,6,7-trimethyl-	C ₁₃ H ₁₄	0.13
Naphthalene, 2-methyl-1-propyl-	C ₁₄ H ₁₆	0.23
Anthracene, 2-methyl-	C ₁₅ H ₁₂	0.11
Phenanthrene, 2,7-dimethyl-	C ₁₆ H ₁₄	0.05
4-Dodecene, (E)-	C ₁₂ H ₂₄	0.89
5-Dodecene, (E)-	C ₁₂ H ₂₄	0.45
6-Dodecene, (E)-	C ₁₂ H ₂₄	0.98
2-Methyl undecane	C ₁₂ H ₂₆	1.32
3-Methyl undecane	C ₁₂ H ₂₆	0.31
2,4-Dimethyl decane	C ₁₂ H ₂₆	0.15

Tridecane	C ₁₃ H ₂₈	0.72
3-Tetradecene, (E)-	C ₁₄ H ₂₈	1.92
Total		100.00

Table S4. Liquid phase GC-MS table of catalytic pyrolysis of LDPE by HY molecular sieve at 500 °C.

component	chemical formula	respective percentages (%)
n-Heptane	C ₇ H ₁₆	1.26
2-Methyl hexane	C ₇ H ₁₆	2.24
3-Methyl hexane	C ₇ H ₁₆	3.28
2,3-Dimethyl pentane	C ₇ H ₁₆	1.08
3-Heptene	C ₇ H ₁₄	1.33
3-Methyl 1-hexene	C ₇ H ₁₄	1.14
4-Methyl 1-hexene	C ₇ H ₁₄	1.43
3-Ethyl pentene	C ₇ H ₁₄	1.52
n-Octane	C ₈ H ₁₈	1.73
2-Methyl heptane	C ₈ H ₁₈	1.09
3-Methyl heptane	C ₈ H ₁₈	1.64
4-Methyl heptane	C ₈ H ₁₈	1.56
3-Ethyl hexane	C ₈ H ₁₈	1.04
2,3-Dimethyl hexane	C ₈ H ₁₈	0.62
2,4-Dimethyl hexane	C ₈ H ₁₈	1.09
2,5-Dimethyl hexane	C ₈ H ₁₈	1.64
3,4-Dimethyl hexane	C ₈ H ₁₈	1.56
3-Ethyl 2-methyl pentane	C ₈ H ₁₈	1.04
2,3,4-Trimethyl pentane	C ₈ H ₁₈	1.22
4-Octene	C ₈ H ₁₆	1.06
n-Nonane	C ₉ H ₂₀	1.24
2-Methyl octane	C ₉ H ₂₀	1.60
3-Methyl octane	C ₉ H ₂₀	1.06
4-Methyl octane	C ₉ H ₂₀	1.24
3-Ethyl heptane	C ₉ H ₂₀	1.60
2,2-Dimethyl heptane	C ₉ H ₂₀	1.60
2,6-Dimethyl heptane	C ₉ H ₂₀	1.02
2,3,5-Trimethyl hexane	C ₉ H ₂₀	1.24

3-Ethyl 2,4-dimethyl pentane	C ₉ H ₂₀	1.30
1-Nonene	C ₉ H ₁₈	2.17
3-Decene	C ₁₀ H ₂₀	2.38
n-Decane	C ₁₀ H ₂₂	1.51
3-Methyl nonane	C ₁₀ H ₂₂	1.85
2,2-Dimethyl octane	C ₁₀ H ₂₂	4.66
2,3-Dimethyl octane	C ₁₀ H ₂₂	1.59
2,5-Dimethyl octane	C ₁₀ H ₂₂	1.42
2,6-Dimethyl octane	C ₁₀ H ₂₂	1.51
2,7-Dimethyl octane	C ₁₀ H ₂₂	1.40
1-Decene	C ₁₀ H ₂₂	0.61
n-Undecane	C ₁₁ H ₂₄	1.24
Dodecane, 4-methyl-	C ₁₃ H ₂₈	2.51
Tridecane	C ₁₃ H ₂₈	2.88
3-Tridecene, (E)-	C ₁₃ H ₂₆	1.02
Toluene	C ₇ H ₈	5.02
Ethylbenzene	C ₈ H ₁₀	0.26
(m,p)-Xylene	C ₈ H ₁₀	5.33
o-Xylene	C ₈ H ₁₀	0.82
Propylbenzene	C ₉ H ₁₂	2.23
1-Ethyl 2-methyl benzene	C ₉ H ₁₂	0.23
1-Ethyl 3-methyl benzene	C ₉ H ₁₂	0.24
1,2,3-Trimethyl benzene	C ₉ H ₁₂	1.18
Cumene	C ₉ H ₁₂	1.91
1,2,4-Trimethyl benzene	C ₉ H ₁₂	0.60
1,3,5-Trimethyl benzene	C ₉ H ₁₂	0.32
2-Ethyl 1,4-dimethyl benzene	C ₁₀ H ₁₄	1.09
2-Ethyl 3,5-dimethyl benzene		0.64
4-Ethyl 1,2-dimethyl benzene	C ₁₀ H ₁₄	1.26
1,2,3,5-Tetramethyl benzene	C ₁₀ H ₁₄	1.04
1,2,4,5-Tetramethyl benzene	C ₁₀ H ₁₄	0.62
1,3-Diethyl 5-methyl benzene	C ₁₁ H ₁₆	0.29
1,1-Dimethyl propylbenzene	C ₁₁ H ₁₆	0.33
2-Methyl 2-propenyl benzene	C ₁₀ H ₁₂	0.26
Naphthalene	C ₁₀ H ₈	2.23
Naphthalene, 2,6-dimethyl-	C ₁₂ H ₁₂	1.76
2-Methyl naphthalene	C ₁₁ H ₁₀	0.65
Naphthalene, 1,6,7-trimethyl-	C ₁₃ H ₁₄	1.95
Chamazulene	C ₁₄ H ₁₆	2.51

Total	100
-------	-----

Table S5. Liquid phase GC-MS table of catalytic pyrolysis of LDPE by MCM-41 molecular sieve at 500 °C.

component	chemical formula	respective percentages (%)
3-Heptene	C ₇ H ₁₄	1.24
3-Methyl 1-hexene	C ₇ H ₁₄	1.23
4-Methyl 1-hexene	C ₇ H ₁₄	1.33
3-Ethyl pentene	C ₇ H ₁₄	2.33
4-Octene	C ₈ H ₁₆	1.23
cis-4-Nonene	C ₉ H ₁₈	1.21
3-Nonene, (E)-	C ₉ H ₁₈	1.24
Cyclopentane, pentyl-	C ₁₀ H ₂₀	1.39
trans-4-Decene	C ₁₀ H ₂₀	2.46
3-Undecene, (E)-	C ₁₁ H ₂₂	1.58
4-Undecene, (Z)-	C ₁₁ H ₂₂	1.15
5-Undecene, (E)-	C ₁₁ H ₂₂	1.37
3-Dodecene, (Z)-	C ₁₂ H ₂₄	1.47
4-Dodecene	C ₁₂ H ₂₄	1.17
5-Dodecene, (E)-	C ₁₂ H ₂₄	1.24
1-Tridecene	C ₁₃ H ₂₆	2.17
3-Tridecene, (Z)-	C ₁₃ H ₂₆	1.24
5-Tridecene, (E)-	C ₁₃ H ₂₆	2.90
3-Tetradecene, (E)-	C ₁₄ H ₂₈	2.27
5-Tetradecene, (E)-	C ₁₄ H ₂₈	2.42
7-Tetradecene, (E)-	C ₁₄ H ₂₈	2.57
Tetradecane	C ₁₄ H ₃₀	2.86
1-Pentadecene	C ₁₅ H ₃₀	3.24

Cetene	C ₁₆ H ₃₂	15.27
Hexadecane	C ₁₆ H ₃₄	8.65
3-Heptadecene, (Z)-	C ₁₇ H ₃₄	3.57
8-Heptadecene	C ₁₇ H ₃₄	2.24
3-Octadecene, (E)-	C ₁₈ H ₃₆	2.24
5-Octadecene, (E)-	C ₁₈ H ₃₆	2.13
1-Nonadecene	C ₁₉ H ₃₈	2.26
3-Eicosene, (E)-	C ₂₀ H ₄₀	12.37
5-Eicosene, (E)-	C ₂₀ H ₄₀	3.26
9-Eicosene, (E)-	C ₂₀ H ₄₀	2.33
Cyclohexadecane, 1,2-diethyl-	C ₂₀ H ₄₀	2.30
Oxalic acid, hexadecyl propyl ester	C ₂₀ H ₄₀	2.12
Total		100