Support Information

Catalytic conversion of furan in the continuous flow fixed-bed reactor

The catalytic reactions were carried out in a continuous flow fixed-bed quartz reactor of ½ in. O.D. ZSM-5 powders were held in the reactor by a quartz frit. The reactor temperature was measured using a K-type thermocouple inserted in an inner tube inserted in the reactor to the top of the catalyst bed. Prior to reactions, the catalyst was calcined as described above. After calcination, the reactor was purged by helium (Airgas, 99.999%) at 408 mL/min for 5 min and cooled down to reaction temperatures. The helium stream then was set to bypass the reactor. Furan and 2MF were introduced into the helium stream by a syringe pump (Fisher KDS100) and was also set to bypass the reactor for 30 min before switching the helium stream to go through the reactor. An air bath condenser was used to trap the heavy products. Gas phase products were collected by air bags. All runs were done at atmospheric pressure. No pressure drop was detected across the catalyst bed.

After reaction, the reactor was purged by helium at a flow rate of 408 mL/min for 45 s at the reaction temperature. The effluent was collected by an air bag. Again, heavy products were trapped in the air bath condenser. After reaction, the spent catalyst was regenerated in-situ at 600°C in a 60 mL/min flowing air. The CO formed during regeneration was converted to CO_2 by a copper catalyst (copper oxide, CuO, Sigma-Aldrich) working at 240°C. CO_2 was trapped by a CO_2 trap (Ascarite, Sigma-Aldrich). The coke yield was obtained by measuring the weight change of the CO_2 trap.

Furfural and FA were fed into the reactor by using a bubbler surrounded by a water bath at 45°C. The helium stream (408 mL/min) flowed through the bubbler and carried furfural or FA vapor into the reactor. The other operations were the same as furan or 2MF conversion.

For olefins co-feeding experiments, a 2% ethylene or a 2% propylene balanced by helium (Airgas) was co-fed into the reactor with different furans feedstocks. Different olefins/furans ratios were obtained by diluting the olefins by another helium stream.

Products analysis

Gas phase products were identified by GC/MS (Shimadzu-2010) and quantified by GC/FID/TCD (Shimadzu-2014). Both GCs are equipped with a Restek Rtx-VMS column. This column cannot separate *p*- and *m*-xylenes. Xylene isomers were separated by using another GC/FID (Shimadzu-2010) equipped with HP-INNOWax column that is able to completely separate all xylene

isomers. The TCD was calibrated by a CO and CO_2 mixture balanced by helium (Airgas, 6% CO_2 and 14% CO). The FID was calibrated by a $C_2 - C_6$ normal olefins standard mixture (Scott Specialty Gas, 1000 ppm for each olefin); furan, benzene, and toluene (Sigma-Aldrich, 99+%, they can be vaporized in airbags filled with helium); prepared liquid standards including xylenes, ethylbenzene, styrene, benzofuran, indene, and naphthalene (Sigma-Aldrich, 99+%). The sensitivity of other compounds was assumed to be proportional to the number of carbon in similar olefins or aromatics (e.g. allene vs propylene, methylindene vs indene).

We also washed the condenser with ethanol and analysed the condensed carbons. In the entire study less than 0.05% of the carbon was obtained in the condenser. The majority of the products were in either the gas phase or coke deposited on the catalyst. Our carbon balance closed with >90% for all runs in this paper unless otherwise mentioned. The reaction time was 4.5 min except for the long time-on-stream reactions.

Table S1. Products distribution obtained from conversions of furan, olefins, and furan + olefins mixtures over ZSM-5.

Feedstock	Furan	Furan	Furan	Furan	Furan	Furan	Furan	Non	Non	Non
Carrier gas	He	He	1.92% Ethylene	1.94% Propylene	2% Propylene	2% Propylene	2% Propylene	1.92% Ethylene	1.94% Propylene	2% propylene
Temperature (°C)	600	600	600	600	550	450	300	600	600	450
Furan WHSV (h^{-1})[a]	10.4	5.9	10.4	10.4	10.4	10.4	10.4	10.4	10.4	9.1
Olefins WHSV (h^{-1})[a]	–	–	11.1	15.6	16.0	16.0	16.0	11.1	15.6	9.1
P_{furan} (torr)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	0.0	0.0	0.0
Olefins/Furan mol. ratio	–	–	2.6	2.4	2.5	2.5	2.5	–	–	–
Furan conversion (%)	48	64	50	65	59	54	14	–	–	–
Olefins conversion (%)	–	–	1	16	25	22	2	4	14	35
Carbon balance (%)	101	105	95	99	99	101	102	98	104	110
Overall selectivity (%)[b]										
CO	13.9	14.1	15.0	7.5	4.4	2.8	0.3	0.0	0.0	0.0
CO_2	1.1	1.8	1.7	1.5	0.8	0.2	0.0	0.0	0.0	0.0
Olefins	19.1	16.9	17.0	29.0	22.7	29.4	31.0	20.2	69.3	86.9
Aromatics	29.2	42.6	40.2	53.8	65.6	60.2	34.5	21.2	22.9	8.9
Coke	33.8	23.0	23.9	7.4	5.5	5.4	19.0	58.6	7.7	4.1
Oxygenates	2.9	1.6	2.1	0.7	1.1	2.0	15.3[c]	0.0	0.0	0.0
Aromatic selectivity (%)										
Benzene	27.5	24.3	28.4	15.3	8.4	5.1	1.9	31.8	35.9	9.6
Toluene	25.1	21.8	30.1	58.6	53.7	38.9	20.9	13.4	32.7	35.1
Xylenes	4.6	3.9	7.9	13.6	18.3	35.1	47.1	3.5	14.8	43.5
Styrene	8.7	5.0	7.1	5.4	4.3	0.8	0.0	5.2	1.8	0.0
Indene	14.2	15.3	9.9	2.6	3.6	2.0	1.6	22.0	5.4	0.0
Naphthalene	7.4	15.2	3.8	0.6	1.6	0.6	0.6	8.5	2.6	0.0
Alkylbenzenes[d]	1.3	0.5	2.1	1.8	4.2	10.3	19.7	0.7	0.9	11.8
Methylstyrene	1.1	0.9	2.5	0.5	0.8	0.3	0.0	0.6	0.4	0.0
Indane	1.7	1.6	2.6	0.7	2.3	3.6	3.9	2.9	0.7	0.0
Methylindene	4.7	7.5	3.3	0.6	2.5	2.3	2.9	6.9	3.7	0.0
Dihydronaphthalene	0.6	1.0	0.1	0.0	0.0	0.1	0.0	0.3	0.0	0.0
Methylnaphthalene	3.2	2.9	2.2	0.2	0.5	1.1	1.3	4.1	1.1	0.0
Olefin selectivity (%)										
Ethylene	38.7	41.7	–	56.4	47.1	29.5	10.3	–	53.8	29.2
Propylene	35.1	35.6	59.1	–	–	–	–	24.4	–	–
C_4 olefins	4.3	4.6	10.4	32.3	39.6	48.2	58.9	71.9	44.8	55.9
Allene	4.6	4.3	4.5	0.7	0.1	0.0	0.0	0.6	0.7	0.0
C_5 olefins	14.2	11.3	19.2	7.1	5.2	7.1	17.4	3.0	0.7	8.9
C_6 olefins	3.1	2.5	6.8	3.6	6.1	11.6	12.0	0.0	0.1	4.8
C_7 olefins	0.0	0.0	0.0	0.0	1.9	3.6	1.5	0.0	0.0	1.2
Xylenes distribution (%)										
p-Xylene	NA	36	NA	NA	NA	NA	NA	NA	NA	37
m-Xylene	NA	47	NA	NA	NA	NA	NA	NA	NA	47
o-Xylene	NA	17	NA	NA	NA	NA	NA	NA	NA	16

[a] Weight hourly space velocity (WHSV) is defined as flow rate of furan, ethylene, or propylene (g/h) divided by weight of the catalyst (g).
[b] For conversion of mixtures, ethylene or propylene are excluded.
[c] Oxygenates includes 86% C_7 oxygenates formed directly by addition of furan and propylene. In the other runs most oxygenates are benzofuran (>50%).
[d] Alkylbenzenes includes ethylbenzene, 1,2,4-trimethylbenzene, 4-ethyltoluene, and propylbenzene.

Table S2. Products distribution obtained from conversion of 2MF (2-methylfuran) and 2MF + propylene mixtures over ZSM-5.

Feedstock	2MF	2MF	2MF	2MF	2MF	2MF	2MF
Carrier gas	He	2% propylene	2% propylene	2% propylene	2% propylene	2% propylene	2% propylene
Temperature (°C)	600	600	450	300	200	450	450
2MF WHSV (h^{-1})[a]	5.7	5.7	5.7	5.7	5.7	5.7	5.7
Propylene WHSV (h^{-1})[a]	–	9.1	9.1	9.1	9.1	2.9	1.0
P_{2MF} (torr)	4.9	4.9	4.9	4.9	4.9	4.9	4.9
Olefins/2MF molar ratio	–	3.09	3.09	3.09	3.09	1.00	0.35
2MF conversion (%)	98	99	92	13	0	86	79
Propylene conversion (%)	–	31	42	20	14	43	35
Carbon Balance (%)	103	99	98	98	97	94	85
Overall selectivity (%)[b]							
CO	11.0	5.9	1.2	0.0	0.0	3.0	4.8
CO_2	0.5	0.1	0.2	0.0	0.0	0.8	1.5
Olefins	23.3	27.8	27.5	23.5	14.4	11.7	8.9
Aromatics	47.3	59.6	66.1	51.7	20.6	71.1	60.4
Coke	16.6	6.2	5.0	24.8	65.0	12.1	21.6
Oxygenates[c]	1.4	0.4	0.0	0.0	0.0	1.3	2.8
Aromatic selectivity (%)							
Benzene	23.8	24.4	6.8	0.9	1.8	6.9	7.4
Toluene	24.5	28.6	17.5	9.2	5.1	17.1	17.3
Xylenes	9.2	26.9	48.9	51.3	35.7	46.5	35.7
Styrene	2.8	1.5	0.4	0.0	0.5	0.9	1.8
Indene	11.0	4.0	1.9	0.5	5.9	2.4	5.3
Naphthalene	7.2	2.4	0.7	0.6	10.7	0.9	1.1
Alkylbenzenes[d]	2.2	4.0	18.2	34.2	34.4	16.4	15.1
Methylstyrene	2.0	1.1	0.4	0.0	0.0	1.3	2.3
Indane	4.5	2.9	3.3	2.4	5.0	5.0	9.4
Methylindene	9.9	3.4	1.6	0.5	0.0	2.0	4.0
Dihydronaphthalene	0.5	0.1	0.0	0.0	0.0	0.0	0.0
Methylnaphthalene	2.4	0.6	0.3	0.4	1.0	0.7	0.6
Olefin selectivity (%)							
Ethylene	28.7	61.6	30.4	9.1	0.0	47.1	56.7
Propylene	35.0	–	–	–	–	–	–
C_4 olefins	15.6	28.0	49.3	61.2	61.9	40.3	30.1
Allene	0.3	0.1	0.0	0.0	0.0	0.0	0.0
C_5 olefins	17.4	7.3	8.0	20.2	18.3	5.7	5.2
C_6 olefins	3.0	3.0	8.6	9.5	19.9	5.2	6.7
C_7 olefins	0.0	0.0	3.7	0.0	0.0	1.7	1.3
Xylenes distribution (%)							
p-Xylene	36	32	43	54	NA	41	43
m-Xylene	46	49	42	37	NA	45	43
o-Xylene	17	19	14	9	NA	14	13

[a] Weight hourly space velocity (WHSV) is defined as flow rate of 2MF or propylene (g/h) divided by weight of the catalyst (g).
[b] For conversion of mixtures, ethylene or propylene are excluded.
[c] Oxygenates contain furan and furylethylene.
[d] Alkylbenzenes includes ethylbenzene, 1,2,4-trimethylbenzene, 4-ethyltoluene, and propylbenzene.

Table S3. Products distribution obtained from conversion of furfural, furfural + propylene mixtures, FA (furfuryl alcohol), and FA + propylene mixtures over ZSM-5.

Feedstock Carrier gas	Furfural He	Furfural 2% propylene	Furfural 2% propylene	FA He	FA 2% propylene
Temperature (°C)	600	600	450	600	600
Furans WHSV (h^{-1})[9]	9.0	9.0	9.0	3.3	3.3
Propylene WHSV (h^{-1})[a]	–	9.1	9.1	9.1	9.1
$P_{furfural\ or}\ P_{FA}$ (torr)[10]	7.0	7.0	7.0	2.5	2.5
Olefins/Furfural or FA molar ratio	–	2.15	2.15	–	6.43
Furfural and FA conversion (%)	100	100	100	100	100
Propylene conversion (%)	–	53	64	–	29
Carbon Balance (%)	31	79	75	26	79
Overall selectivity (%)[11]					
CO	29.3	11.3	7.3	13.0	2.0
CO_2	3.3	1.9	0.1	1.5	0.0
Olefins	18.8	38.7	46.6	14.7	58.5
Aromatics	16.7	42.7	38.6	42.4	34.4
Coke	16.6	3.4	2.9	25.8	4.8
Oxygenates[12]	15.2	2.0	4.5	2.6	0.3
Aromatic selectivity (%)					
Benzene	35.5	21.0	6.1	9.1	23.4
Toluene	28.6	57.9	38.5	13.1	38.2
Xylene	6.9	14.2	38.5	13.3	21.7
Styrene	6.3	1.9	0.5	7.4	3.1
Indene	8.2	1.5	1.0	17.8	2.9
Naphthalene	8.1	1.2	0.6	12.5	3.1
Alkylbenzenes[13]	0.6	1.0	10.2	4.4	3.3
Methylstyrene	0.6	0.2	0.1	2.2	0.4
Indane	0.6	0.3	2.9	5.6	1.5
Methylindene	2.5	0.5	1.4	10.0	1.8
Dihydronaphthalene	0.4	0.0	0.0	0.4	0.0
Methylnaphthalene	1.8	0.4	0.3	4.2	0.6
Olefin selectivity (%)					
Ethylene	38.1	58.3	28.6	43.5	55.8
Propylene	42.8	–	–	36.1	–
C_4 olefins	8.2	35.6	55.4	12.5	40.9
Allene	4.5	0.0	0.0	3.2	0.0
C_5 olefins	5.8	5.1	7.9	4.7	2.4
C_6 olefins	0.62	1.0	6.0	0.0	0.9
C_7 olefins	0.0	0.0	2.07	0.0	0.0
Xylenes distribution (%)					
p-Xylene	37	32	40	40	31
m-Xylene	46	51	46	43	49
o-Xylene	17	18	14	17	20

[9] Weight hourly space velocity (WHSV) is defined as flow rate of furfural or propylene (g/h) divided by weight of the catalyst (g). The amount of furfural was estimated by Antoine Equation at 45°C.

[10] The vapor pressure of furfural was estimated by Antoine Equation at 45°C.

[11] For conversion of mixtures, ethylene or propylene are excluded.

[12] Oxygenates contain 97 – 99% furan and 1 – 3% 2MF

[13] Alkylbenzenes includes ethylbenzene, 1,2,4-trimethylbenzene, 4-ethyltoluene, and propylbenzene.