

Supporting information

Table S1. Exchange ratios of zeolites synthesized in this study.

Catalyst	M/Al Molar Ratio
Na-MOR	0.51
Na-ZSM5	0.54
Na-BEA	0.66
Na-Y	0.61
Li-BEA	0.20
K-BEA	0.41
Rb-BEA	0.53
Cs-BEA	0.72

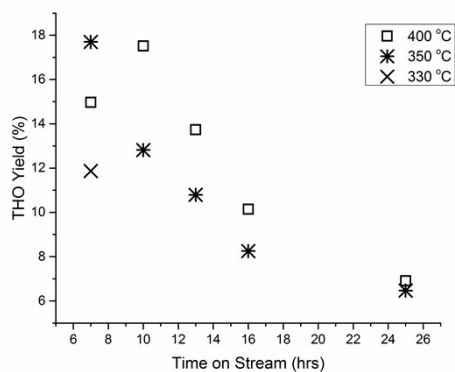


Figure S1. Study of THO yields from THP2M over a range of temperatures. The reaction at 330 °C was stopped due to very low yield (and selectivity) to THO. Reaction conditions: 0.628 mL/hr THP2M (liquid flow rate, STP), 30 mL/min (STP) H₂, 1 atm, 150 mg amorphous SiO₂-Al₂O₃. Results are not shown for reactions above 400 °C, as carbon balances decreased sharply in this regime due to a large increase in yields of gas-phase species.

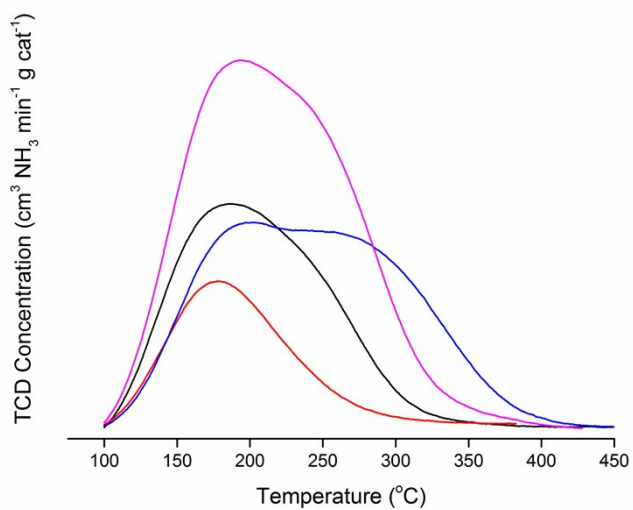


Figure S2. NH₃-TPD of Na-exchanged BEA (black), Y (red), ZSM-5 (blue), and MOR (pink). Ramp rate = 10 °C/min

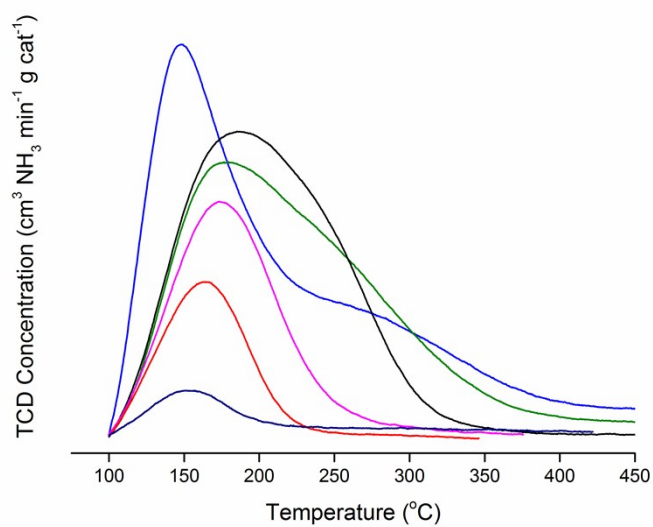


Figure S3. NH₃-TPD of BEA exchanged with Li (green), Na (black, same as Fig. S3), K (pink), Rb (red), Cs (navy). Parent catalyst H-BEA shown in blue. Ramp rate = 10 °C/min

Table S2. Fraction of mass lost in spent catalyst during TPO experiments

Catalyst	Mass Loss During Calcination of Spent Catalyst (%)
Na-MOR	16.1
Na-ZSM5	19.0
Na-Y	27.9
Na-BEA	36.5
H-BEA	30.2
Li-BEA	36.2
K-BEA	26.3
Rb-BEA	22.7
Cs-BEA	19.4

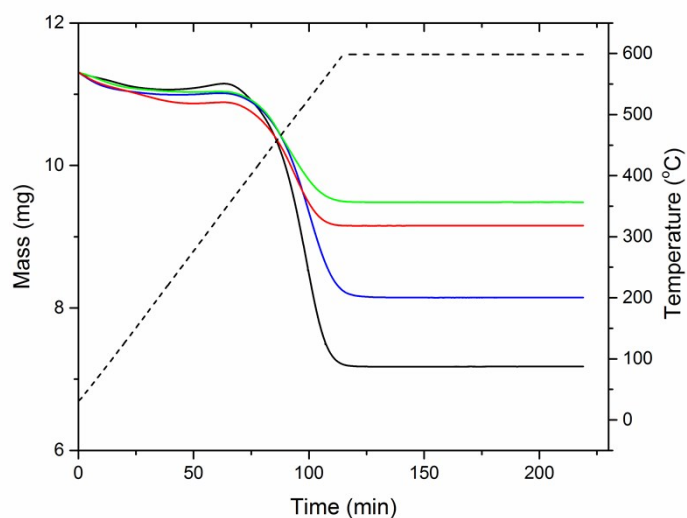


Figure S4. TGA curves of spent Na-exchanged BEA (black curve), Y (blue curve), ZSM5 (green curve), and MOR (red curve). Spent catalysts were heated at 5 °C/min under 20 mL/min air. Dashed Line represents sample temperature. The initial catalyst mass was normalized to the same value for each catalyst. In reality, the starting mass for all spent catalysts was 10-12 mg.

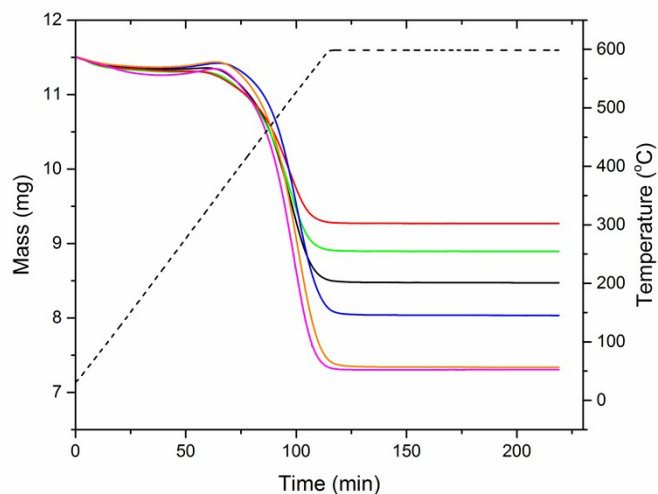


Figure S5. TGA curves of spent BEA exchanged with H⁺ (blue curve), Li⁺ (orange curve), Na⁺ (pink curve), K⁺ (black curve), Rb⁺ (green curve), and Cs⁺ (red curve). Spent catalysts were heated at 5 °C/min under 20 mL/min air. Dashed Line represents sample temperature. The initial catalyst mass was normalized to the same value for each catalyst. In reality, the starting mass for all spent catalysts was 10-12 mg.

Table S3. DFT-optimized (B3LYP/G def2-SVP) C-O-C bond angles and lengths for each oxygen site in DBO, in comparison with the C-O-C bond angles of seven-membered oxepane (OXE) and five-membered tetrahydrofuran (THF).

Molecule	C-O-C bond angle in seven-membered ring (°)	C-O-C bond angle in five-membered ring (°)	C-O bond length in seven-membered ring (Å)	C-O bond length in five-membered ring (Å)
DBO	112.5	102.6	1.419	1.432
OXE	114.9	-	1.413	-
THF	-	110.6	-	1.423

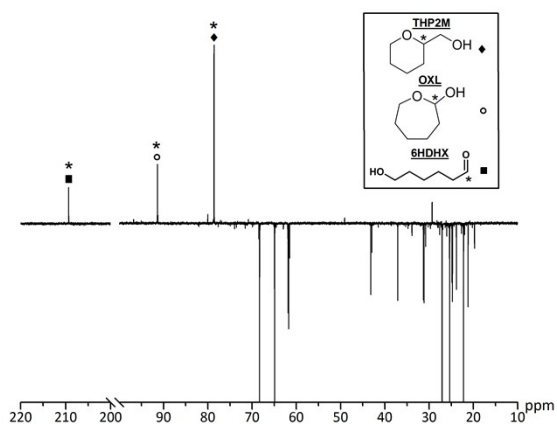


Figure S6. Dept. 135 NMR spectra of reaction solution formed via hydration of THP2M dehydration product.

Table S4. Complete list of abbreviations used in this article.

Compound	Abbreviation
2,3,4,5-tetrahydrooxepine	THO
Tetrahydropyran-2-methanol	THP2M
1,6-hexanediol	1,6-HDO
Tetrahydropyran-2-carbaldehyde	THP2C
6,8-dioxabicyclooctane	DBO
Dihydromethylpyran	DMP
Cyclopentanecarbaldehyde	CPC
Oxepane	OXE
2-methylcyclopentanone	2MCP
2-oxepanol	OXL
6-hydroxyhexanal	6HDHX
1,3-cyclohexadiene	13CDE
1,4-cyclohexadiene	14CDE
Cyclohexene	CXE
Cyclohexanone	CXO
2-methyltetrahydropyran	2MTHP
2-methylenetetrahydropyran	2METHP
6-tetrahydropyran-1-hexanol	6THP-1H

Table S5. Dehydration of THP2M over Na-Y. Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate), 30 mL/min H₂, 1 atm, 150 mg catalyst.

Time on Stream (hrs)	Conversion (%)	DMP Yield (%)	5-hexenal (%)	3-hexenal (%)	2-hexenal (%)	CPC (%)	2MCP (%)	OXE (%)	THP2C (%)	DBO (%)	2METHP (%)	5-hexen-1-ol (%)	4-hexen-1-ol (%)	13CDE (%)	14CDE (%)	CXE (%)	CXO (%)	2MTHP (%)	6THP-1H (%)	THO (%)	Carbon Balance (%)
4	56.18	2.33	2.40	1.25	0.50	2.71	2.01	2.04	1.68	0.55	0.50	0.26	0.11	0.72	0.40	1.41	0.22	0.29	0.08	19.32	82.59
7	36.06	1.66	1.10	0.41	0.17	1.51	1.63	0.81	1.29	0.66	0.29	0.09	0.04	0.19	0.07	0.24	0.09	0.06	0.09	16.50	90.84
10	32.32	1.33	0.74	0.20	0.09	1.14	1.47	0.55	1.01	0.68	0.19	0.05	0.03	0.11	0.03	0.14	0.06	0.03	0.03	13.44	89.01
13	27.62	1.17	0.61	0.15	0.07	1.00	1.38	0.46	0.93	0.74	0.17	0.04	0.03	0.09	0.07	0.11	0.05	0.03	0.03	11.75	91.28
25	19.53	0.88	0.44	0.09	0.04	0.78	1.47	0.31	0.79	1.09	0.12	0.01	0.01	0.06	0.09	0.07	0.03	0.01	0.02	8.98	95.76

Table S6. Dehydration of THP2M over Na-ZSM5. Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate), 30 mL/min H₂, 1 atm, 150 mg catalyst.

Time on Stream (hrs)	Conversion (%)	DMP Yield (%)	5-hexenal (%)	3-hexenal (%)	2-hexenal (%)	CPC (%)	2MCP (%)	OXE (%)	THP2C (%)	DBO (%)	2METHP (%)	5-hexenol (%)	4-hexenol (%)	13CDE (%)	14CDE (%)	CXE (%)	CXO (%)	2MTHP (%)	6THP-1H (%)	THO (%)	Carbon Balance (%)
4	60.23	1.46	2.09	2.04	1.52	3.65	2.86	0.80	1.55	0.66	1.23	1.05	0.10	2.44	0.63	2.33	0.30	0.18	0.13	12.88	77.65
7	47.76	1.47	2.05	1.28	0.66	2.61	2.43	0.55	1.12	0.76	0.33	0.16	0.05	0.67	0.13	0.53	0.18	0.03	0.08	15.44	82.78
10	32.16	0.75	0.89	0.20	0.00	0.69	1.49	0.25	0.64	1.53	0.10	0.01	0.00	0.08	0.06	0.13	0.05	0.01	0.03	10.79	85.53
13	21.73	0.88	1.13	0.62	0.20	1.25	1.57	0.28	0.71	1.37	0.14	0.05	0.01	0.22	0.09	0.23	0.09	0.02	0.01	7.97	95.11
16	18.61	0.64	0.76	0.42	0.13	0.77	1.64	0.18	0.54	1.53	0.09	0.00	0.03	0.15	0.07	0.16	0.06	0.00	0.01	5.14	93.68
25	11.64	0.43	0.52	0.26	0.03	0.45	0.77	0.11	0.45	1.55	0.05	0.00	0.00	0.08	0.05	0.08	0.03	0.00	0.00	3.24	96.47

Table S7. Dehydration of THP2M over Na-MOR. Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate), 30 mL/min H₂, 1 atm, 150 mg catalyst.

Time on Stream (hrs)	Conversion (%)	DMP Yield (%)	5-hexenal (%)	3-hexenal (%)	2-hexenal (%)	CPC (%)	2MCP (%)	OXE (%)	THP2C (%)	DBO (%)	2METHP (%)	5-hexen-1-ol (%)	4-hexen-1-ol (%)	13CDE (%)	14CDE (%)	CXE (%)	CXO (%)	2MTHP (%)	6THP-1H (%)	THO (%)	Carbon Balance (%)
4	62.69	2.37	3.92	1.58	0.63	4.53	1.99	1.61	1.68	0.39	0.61	0.25	0.09	0.74	0.33	1.62	0.40	0.24	0.67	22.07	83.04
7	47.46	1.76	2.68	0.56	0.42	0.86	1.38	0.37	1.45	2.63	0.36	0.11	0.07	0.19	0.07	0.33	0.15	0.08	0.50	20.76	87.28
10	25.86	0.93	1.21	0.27	0.04	1.38	0.79	0.35	0.73	0.42	0.13	0.08	0.03	0.11	0.05	0.23	0.06	0.04	0.04	9.27	90.31
13	14.53	0.81	0.94	0.22	0.05	1.04	0.73	0.30	0.69	0.56	0.11	0.09	0.06	0.10	0.04	0.19	0.05	0.03	0.05	7.45	98.98
16	18.59	0.58	0.67	0.15	0.07	0.62	0.54	0.20	0.53	0.48	0.11	0.05	0.01	0.06	0.03	0.13	0.03	0.02	0.03	5.17	90.89
25	6.57	0.46	0.47	0.20	0.00	0.49	0.42	0.15	0.52	0.52	0.06	0.05	0.03	0.05	0.03	0.10	0.02	0.02	0.02	3.38	100.42

Table S8. Dehydration of THP2M over Na-BEA. Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate), 30 mL/min H₂, 1 atm, 150 mg catalyst.

Time on Stream (hrs)	Conversion (%)	DMP Yield (%)	5-hexenal (%)	3-hexenal (%)	2-hexenal (%)	CPC (%)	2MCP (%)	OXE (%)	THP2C (%)	DBO (%)	2METHP (%)	5-hexen-1-ol (%)	4-hexen-1-ol (%)	13CDE (%)	14CDE (%)	CXE (%)	CXO (%)	2MTHP (%)	6THP-1H (%)	THO (%)	Carbon Balance (%)
4	81.46	2.95	3.29	1.32	0.84	6.58	3.13	3.38	2.36	0.66	0.86	0.48	0.25	1.73	0.45	2.17	0.55	0.39	0.91	23.70	74.52
7	60.50	2.21	1.93	0.67	0.36	3.86	1.85	1.39	1.87	0.33	0.44	0.19	0.08	0.66	0.18	0.86	0.22	0.12	0.83	23.69	81.24
10	45.57	1.82	1.47	0.48	0.25	2.87	1.57	0.91	1.55	0.39	0.33	0.14	0.06	0.47	0.15	0.65	0.14	0.07	0.55	19.30	87.60
13	39.33	1.54	1.19	0.35	0.20	2.37	1.26	0.70	1.28	0.40	0.28	0.12	0.05	0.37	0.09	0.51	0.11	0.06	0.38	15.39	87.33
16	32.29	1.31	0.99	0.27	0.14	1.97	1.09	0.51	1.07	0.38	0.22	0.08	0.03	0.28	0.08	0.41	0.08	0.04	0.26	13.69	90.61
25	23.11	1.06	0.81	0.19	0.04	1.53	0.86	0.67	0.82	0.41	0.16	0.06	0.03	0.19	0.06	0.30	0.05	0.03	0.09	10.58	94.83

Table S9. Dehydration of THP2M over H-BEA. Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate), 30 mL/min H₂, 1 atm, 150 mg catalyst.

Time on Stream (hrs)	Conversion (%)	DMP Yield (%)	5-hexenal (%)	3-hexenal (%)	2-hexenal (%)	CPC (%)	2MCP (%)	OXE (%)	THP2C (%)	DBO (%)	2METHP (%)	5-hexen-1-ol (%)	4-hexen-1-ol (%)	13CDE (%)	14CDE (%)	CXE (%)	CXO (%)	2MTHP (%)	6THP-1H (%)	THO (%)	Carbon Balance (%)
4	94.83	3.38	6.00	3.39	1.18	7.42	3.47	2.80	1.91	0.48	0.87	0.54	0.20	2.56	1.18	5.64	0.84	0.42	0.41	25.10	72.98
7	77.99	3.39	4.31	1.65	0.68	4.08	2.47	2.47	1.84	0.42	0.61	0.29	0.16	0.74	0.43	1.13	0.61	0.24	1.77	29.31	78.62
10	67.02	3.04	3.29	1.15	0.47	2.94	2.04	1.82	1.71	0.35	0.49	0.21	0.12	0.51	0.28	0.94	0.42	0.16	1.53	27.85	82.29
13	64.67	3.22	3.53	1.04	0.42	2.74	1.89	1.47	1.47	0.31	0.49	0.18	0.10	0.38	0.20	0.68	0.38	0.12	0.97	32.52	87.46
16	56.39	2.90	2.92	0.82	0.34	2.21	1.67	1.19	1.35	0.26	0.42	0.13	0.08	0.31	0.13	0.48	0.29	0.09	0.74	29.73	89.67
25	27.58	1.96	1.74	0.51	0.07	1.29	1.26	0.74	1.03	0.27	0.27	0.09	0.00	0.20	0.10	0.30	0.16	0.06	0.45	15.99	98.91

Table S10. Dehydration of THP2M over Li-BEA. Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate), 30 mL/min H₂, 1 atm, 150 mg catalyst.

Time on Stream (hrs)	Conversion (%)	DMP Yield (%)	5-hexenal (%)	3-hexenal (%)	2-hexenal (%)	CPC (%)	2MCP (%)	OXE (%)	THP2C (%)	DBO (%)	2METHP (%)	5-hexen-1-ol (%)	4-hexen-1-ol (%)	13CDE (%)	14CDE (%)	CXE (%)	CXO (%)	2MTHP (%)	6THP-1H (%)	THO (%)	Carbon Balance (%)
4	85.91	3.37	3.86	1.81	0.76	6.23	3.85	2.86	2.08	0.61	0.83	0.45	0.21	2.16	0.82	3.07	0.69	0.35	0.41	29.33	77.84
7	66.51	2.75	2.47	0.73	0.23	3.55	3.19	1.28	1.57	0.42	0.34	0.10	0.04	0.73	0.31	0.96	0.29	0.07	0.56	27.74	80.85
10	52.88	2.40	1.97	0.61	0.24	2.64	3.15	0.97	1.51	0.64	0.36	0.14	0.06	0.49	0.32	0.70	0.20	0.07	0.41	24.06	88.08
13	45.69	1.99	1.55	0.45	0.11	1.88	2.77	0.68	1.19	0.64	0.28	0.06	0.02	0.35	0.27	0.52	0.14	0.04	0.26	20.05	87.57
16	29.97	1.05	0.83	0.22	0.02	1.09	1.89	0.32	0.86	1.23	0.12	0.01	0.00	0.25	0.22	0.46	0.07	0.02	0.02	9.05	87.76
25	43.13	1.65	4.12	0.65	0.27	1.89	2.05	1.36	1.90	0.49	0.36	0.16	0.07	0.27	0.19	0.36	0.14	0.15	0.98	17.85	91.78

Table S11. Dehydration of THP2M over K-BEA. Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate), 30 mL/min H₂, 1 atm, 150 mg catalyst.

Time on Stream (hrs)	Conversion (%)	DMP Yield (%)	5-hexenal (%)	3-hexenal (%)	2-hexenal (%)	CPC (%)	2MCP (%)	OXE (%)	THP2C (%)	DBO (%)	2METHP (%)	5-hexenol (%)	4-hexenol (%)	13CDE (%)	14CDE (%)	CXE (%)	CXO (%)	2MTHP (%)	6THP-1H (%)	THO (%)	Carbon Balance (%)
4	90.48	3.80	4.87	1.81	0.84	7.34	3.54	2.87	1.97	0.58	0.87	0.43	0.20	1.45	0.44	1.87	0.82	0.27	0.08	37.52	81.10
7	79.68	3.45	2.95	0.76	0.37	4.81	3.03	1.79	1.69	0.40	0.54	0.16	0.08	0.53	0.08	0.42	0.43	0.08	0.31	39.88	82.07
10	58.03	2.25	1.80	0.51	0.23	2.64	2.69	1.05	1.52	0.58	0.38	0.13	0.06	0.31	0.12	0.33	0.21	0.06	0.39	26.69	83.93
13	58.48	2.70	1.85	0.50	0.24	3.26	2.87	1.21	1.55	0.39	0.43	0.12	0.06	0.29	0.07	0.23	0.22	0.06	0.31	25.59	83.46
16	47.64	2.51	1.64	0.30	0.18	2.86	2.98	1.05	1.48	0.39	0.39	0.10	0.05	0.23	0.04	0.17	0.17	0.05	0.28	19.44	86.66
25	38.14	1.35	0.86	0.16	0.05	1.30	2.01	0.46	0.95	0.75	0.20	0.03	0.02	0.13	0.07	0.13	0.08	0.02	0.11	19.77	90.30

Table S12. Dehydration of THP2M over Rb-BEA. Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate), 30 mL/min H₂, 1 atm, 150 mg catalyst.

Time on Stream (hrs)	Conversion (%)	DMP Yield (%)	5-hexenal (%)	3-hexenal (%)	2-hexenal (%)	CPC (%)	2MCP (%)	OXE (%)	THP2C (%)	DBO (%)	2METHP (%)	5-hexen-1-ol (%)	4-hexen-1-ol (%)	13CDE (%)	14CDE (%)	CXE (%)	CXO (%)	2MTHP (%)	6THP-1H (%)	THO (%)	Carbon Balance (%)
4	56.26	2.49	2.27	1.10	0.43	3.29	2.87	1.90	1.91	0.59	0.64	0.23	0.13	0.89	0.45	1.10	0.41	0.19	0.25	17.64	82.54
7	45.52	1.69	1.39	0.47	0.21	2.50	2.30	0.94	1.54	0.83	0.36	0.12	0.08	0.35	0.15	0.34	0.20	0.07	0.20	15.18	83.41
10	37.86	1.05	1.25	0.32	0.10	2.48	1.64	0.68	1.41	0.99	0.26	0.06	0.03	0.29	0.21	0.30	0.14	0.04	0.21	13.45	87.06
13	28.26	1.35	1.08	0.25	0.08	2.30	2.09	0.59	1.35	1.19	0.27	0.04	0.02	0.22	0.20	0.24	0.12	0.03	0.11	13.17	96.44
16	31.88	1.14	0.85	0.19	0.06	1.90	1.76	0.46	1.11	1.20	0.21	0.04	0.03	0.17	0.16	0.18	0.09	0.03	0.05	11.15	88.91
25	28.24	0.93	0.67	0.13	0.02	1.59	1.52	0.33	0.96	1.35	0.17	0.02	0.01	0.12	0.15	0.13	0.06	0.02	0.01	9.23	89.19

Table S13. Dehydration of THP2M over Cs-BEA. Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate), 30 mL/min H₂, 1 atm, 150 mg catalyst.

Time on Stream (hrs)	Conversion (%)	DMP Yield (%)	5-hexenal (%)	3-hexenal (%)	2-hexenal (%)	CPC (%)	2MCP (%)	OXE (%)	THP2C (%)	DBO (%)	2METHP (%)	5-hexen-1-ol (%)	4-hexen-1-ol (%)	13CDE (%)	14CDE (%)	CXE (%)	CXO (%)	2MTHP (%)	6THP-1H (%)	THO (%)	Carbon Balance (%)
4	57.73	0.42	1.98	0.87	0.37	2.93	3.55	1.65	1.76	0.85	0.60	0.24	0.17	0.73	0.20	0.93	0.39	0.15	0.10	19.56	79.71
7	47.69	0.39	0.22	0.21	0.32	0.35	3.16	1.04	1.88	0.70	0.44	0.20	0.05	4.50	0.11	0.43	0.13	0.06	0.05	22.15	88.71
10	40.10	1.50	1.42	0.33	0.22	3.12	2.21	0.99	1.78	0.83	0.40	0.08	0.08	0.23	0.13	0.16	0.17	0.05	0.22	20.12	93.94
13	39.73	0.90	1.10	0.23	0.06	2.59	1.81	0.80	1.46	0.84	0.32	0.03	0.00	0.18	0.17	0.14	0.13	0.04	0.13	18.03	89.24
16	34.08	1.63	1.07	0.21	0.06	2.68	2.24	0.74	1.44	0.91	0.31	0.03	0.00	0.09	0.20	0.03	0.12	0.03	0.11	17.66	95.47
25	25.61	1.16	0.69	0.00	0.00	2.09	1.74	0.46	1.17	1.29	0.22	0.00	0.00	0.10	0.11	0.07	0.09	0.00	0.00	12.62	96.21