Supporting Information

Alkali metal ion exchanged ZSM-5 catalysts: On acidity and methanol-to-olefin performance

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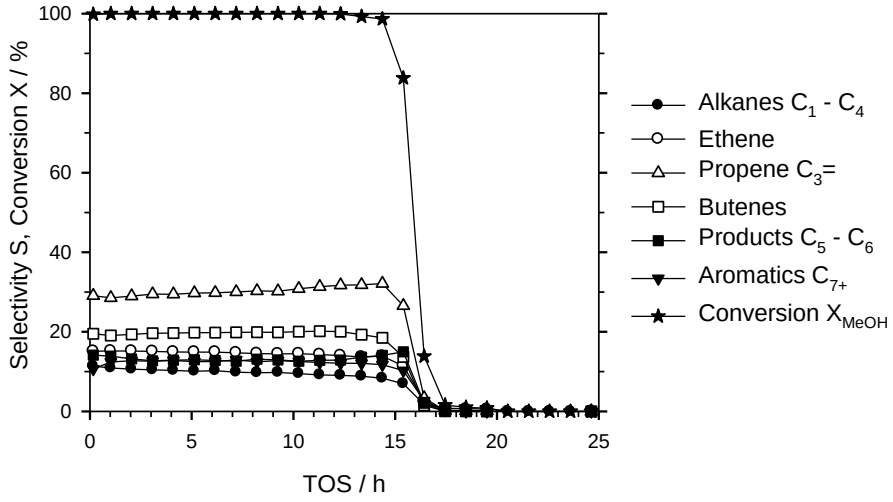

Figure S1: Methanol conversion X and product selectivity S for the Li1-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 63.6 g_{MeOH}/g_{Cat}.

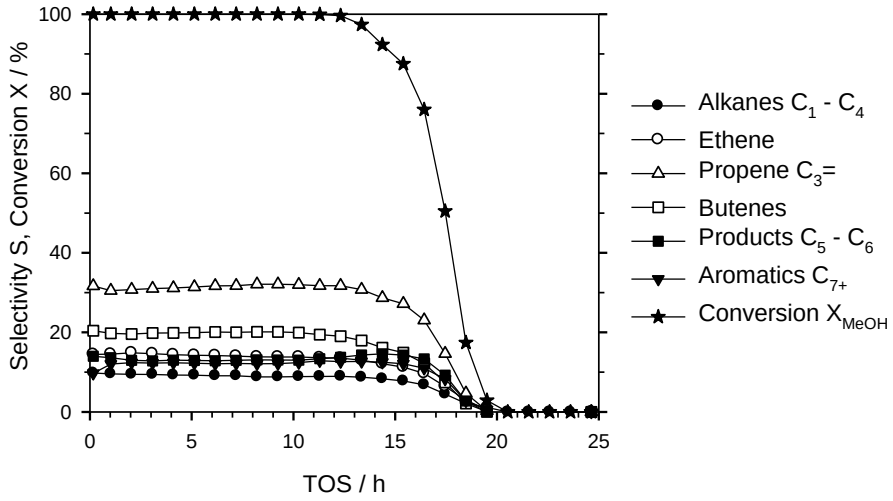

Figure S2: Methanol conversion X and product selectivity S for the Li2-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 68.7 g_{MeOH}/g_{Cat}.

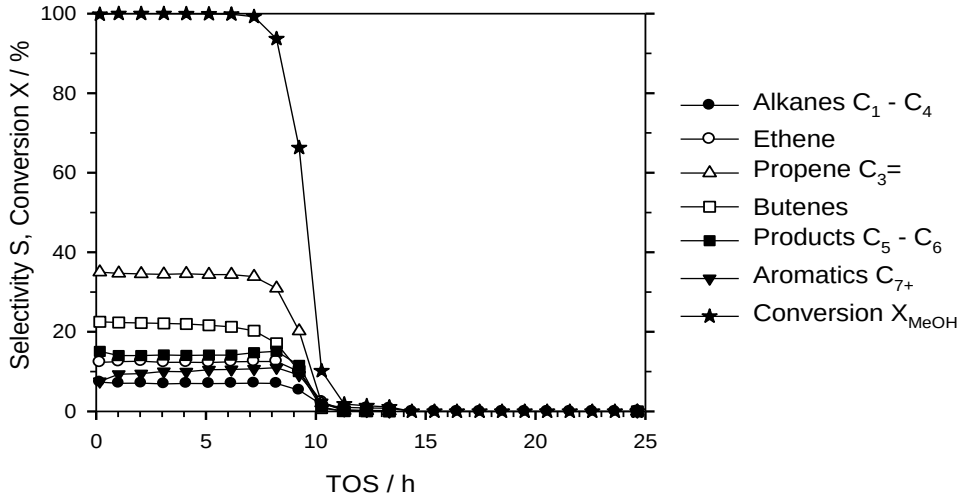

Figure S3: Methanol conversion X and product selectivity S for the Li3-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 37.9 g_{MeOH}/g_{Cat}.

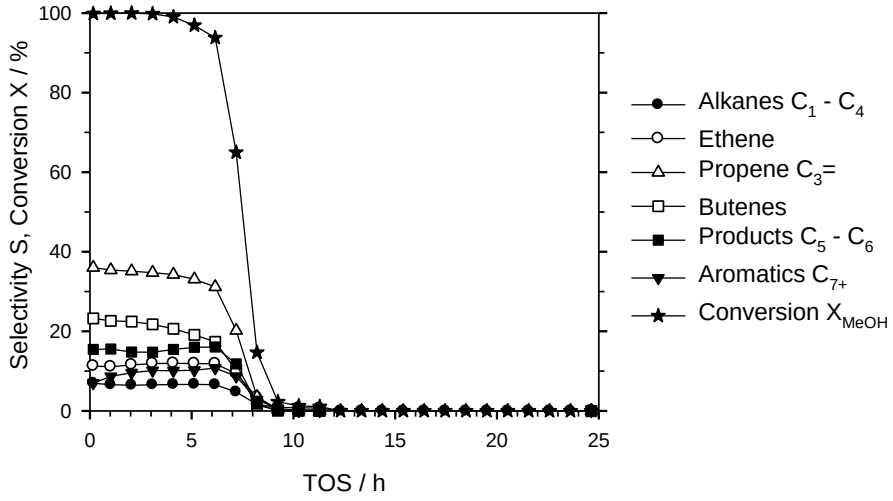

Figure S4: Methanol conversion X and product selectivity S for the Li4-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 29.7 g_{MeOH}/g_{Cat}.

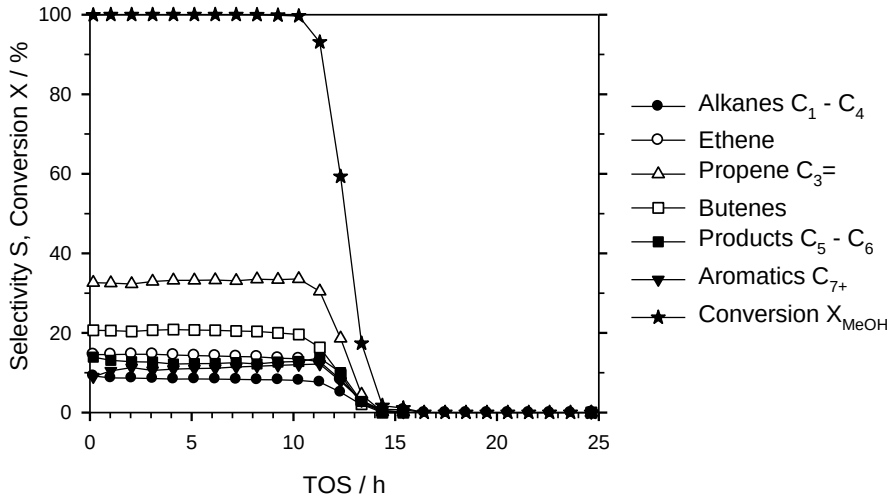

Figure S5: Methanol conversion X and product selectivity S for the Na1-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 50.2 g_{MeOH}/g_{Cat}.

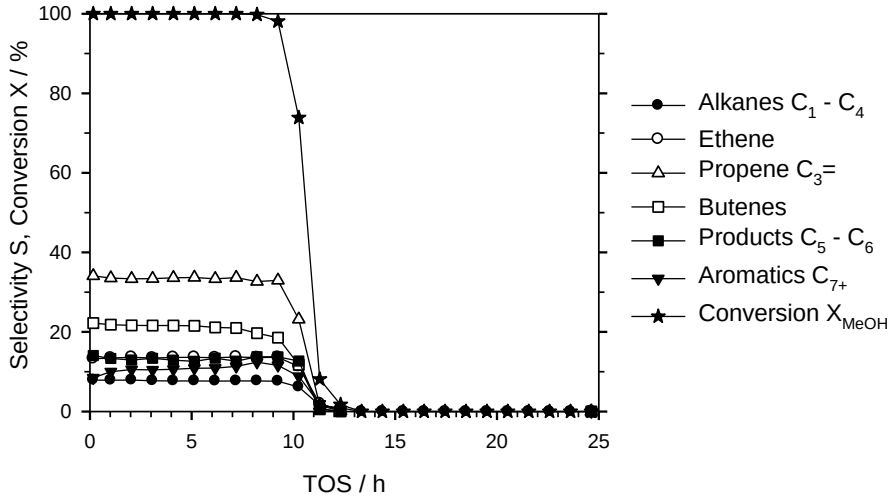

Figure S6: Methanol conversion X and product selectivity S for the Na2-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 42.4 g_{MeOH}/g_{Cat}.

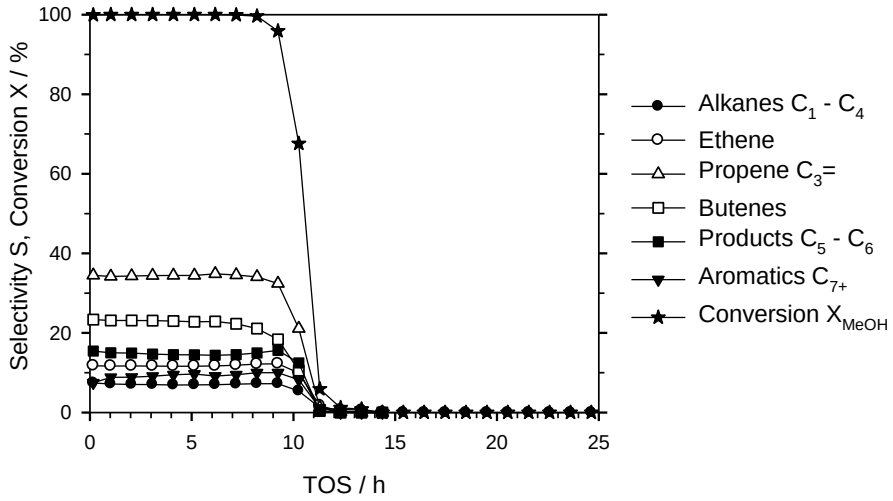

Figure S7: Methanol conversion X and product selectivity S for the Na3-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 41.9 g_{MeOH}/g_{Cat}.

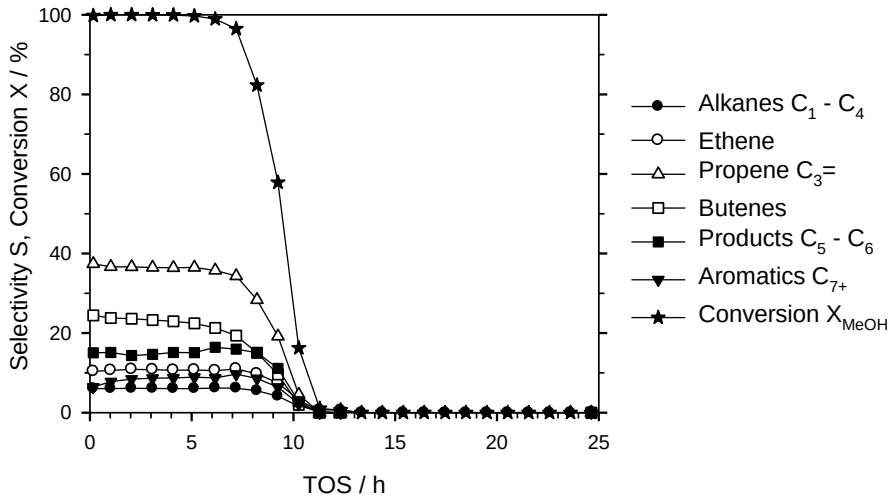

Figure S8: Methanol conversion X and product selectivity S for the Na4-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 37.1 g_{MeOH}/g_{Cat}.

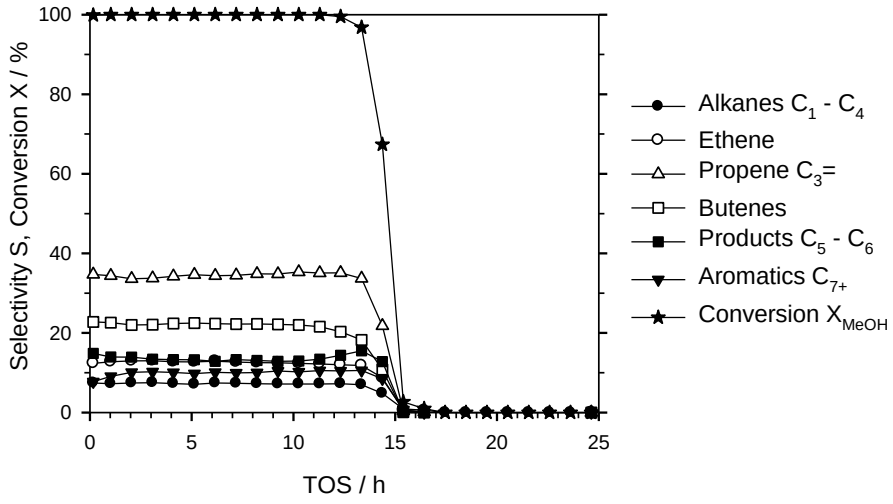

Figure S9: Methanol conversion X and product selectivity S for the Cs1-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 50.0 g_{MeOH}/g_{Cat}.

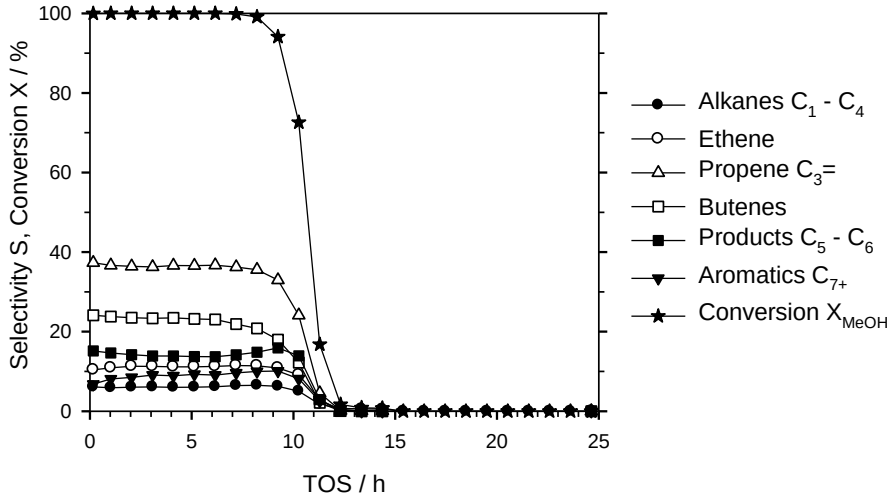

Figure S10: Methanol conversion X and product selectivity S for the Cs2-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 42.4 g_{MeOH}/g_{Cat}.

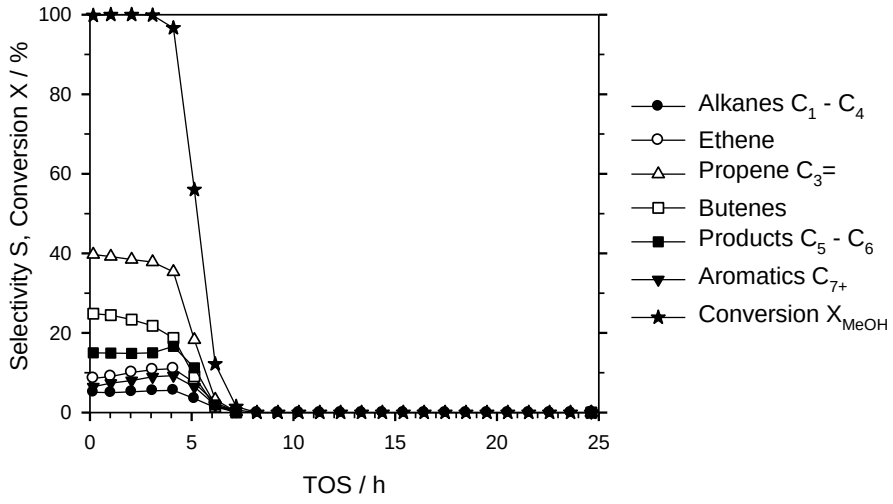

Figure S11: Methanol conversion X and product selectivity S for the Cs3-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 21.2 g_{MeOH}/g_{Cat}.

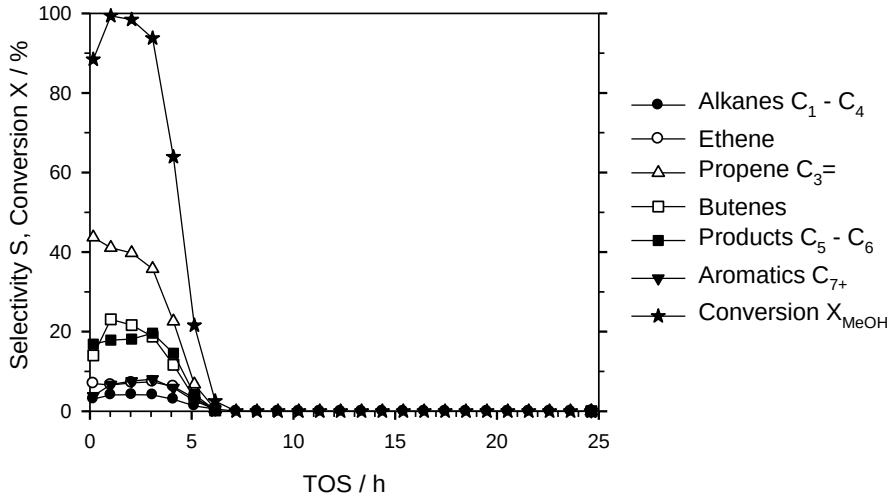

Figure S12: Methanol conversion X and product selectivity S for the Cs4-ZSM-5 catalyst (T = 723 K, WHSV = 4 h^{-1}) with a conversion capacity of 17.3 g_{MeOH}/g_{Cat}.

Table S13: Conversion X, product selectivities S, and descriptive ratios used in Figs. S14 and S15 for comparing the properties of the catalysts under study at ≈ 80% conversion (at T = 723 K, p_{MeOH} = 12.8 kPa, WHSV = 4 h^{-1}).

Catalyst	X	$S_{AlkanesC1-C4}$	S_{Ethene}	$S_{Propene}$	$S_{Butenes}$	S_{C5-C6}	S_{C7+}	$C_3=/C_2=$	$C_3=/C_3$	$(C_2= - C_4=)/(C_1 - C_4)$	HTI C_4
H-ZSM-5	82	8.8	12.4	31.8	17.9	17.7	11.5	2.6	11.7	7.1	0.18
Li1-ZSM-5	84	8.3	13.6	31.7	16.3	17.8	12.2	2.3	17.7	7.4	0.14
Li2-ZSM-5	82	8.9	12.8	30.7	16.5	16.9	14.1	2.4	12.2	6.7	0.17
Li3-ZSM-5	80	7.7	14.1	31.9	17.0	16.7	12.6	2.3	21.9	8.2	0.13
Li4-ZSM-5	79	7.1	13.4	32.3	17.3	17.6	12.3	2.4	23.7	8.8	0.14
Na1-ZSM-5	82	8.3	13.8	32.4	17.2	15.2	13.1	2.4	16.8	7.6	0.13
Na2-ZSM-5	82	8.1	14.8	32.2	17.1	15.9	11.9	2.2	18.3	7.9	0.11
Na3-ZSM-5	77	7.8	13.9	32.3	17.1	17.6	11.4	2.3	20.9	8.1	0.14
Na4-ZSM-5	82	6.7	11.8	34.5	18.3	18.3	10.4	2.9	23.8	9.7	0.12
Cs1-ZSM-5	82	7.2	12.5	33.8	17.7	17.2	11.6	2.7	19.9	8.9	0.11
Cs2-ZSM-5	83	6.8	12.0	34.2	18.1	17.9	11.0	2.9	20.0	9.5	0.10
Cs3-ZSM-5	76	5.9	12.1	35.1	18.3	18.3	10.3	2.9	28.3	11.0	0.09
Cs4-ZSM-5	79	4.5	8.6	37.0	19.3	21.7	8.9	4.3	44.6	14.4	0.09

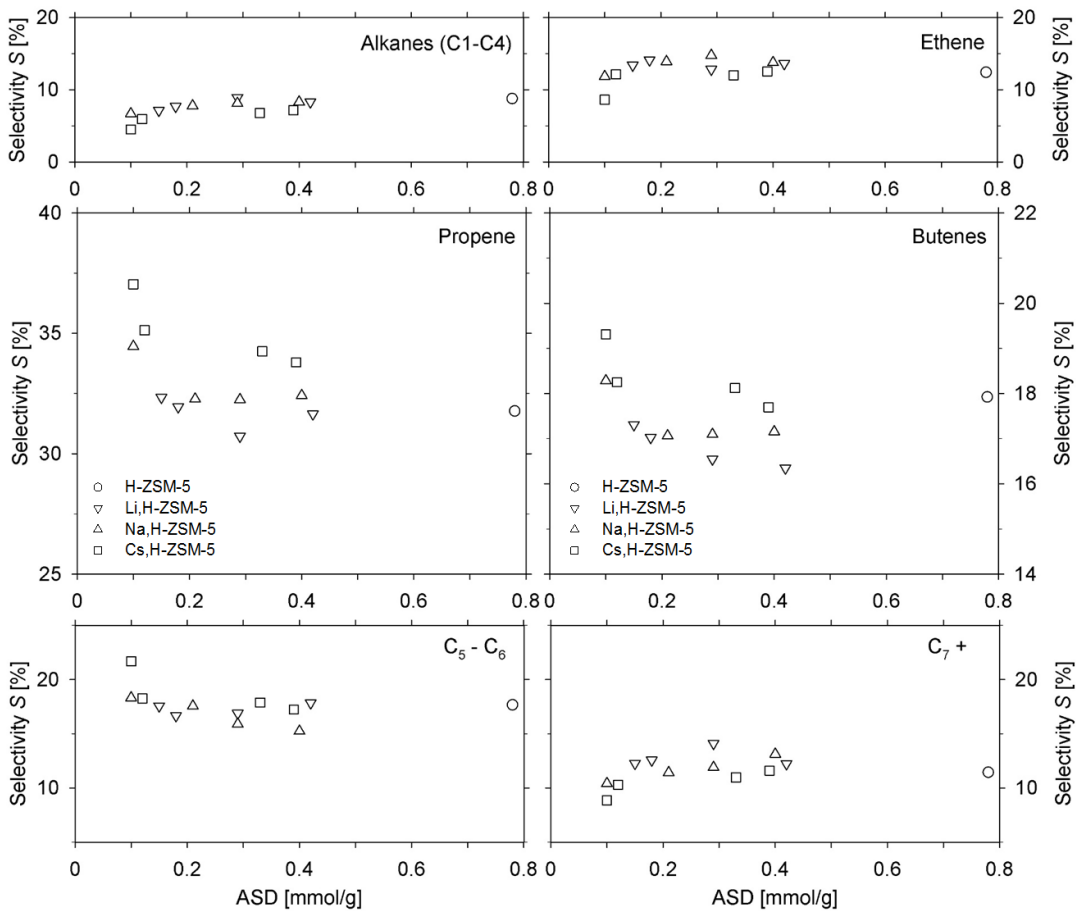

Figure S14: MTO selectivity S of reaction products as function of the acid site density (ASD) of the parent H-ZSM-5 and modified Li,H-; Na,H-; and Cs,H-ZSM-5 catalysts ($X \approx 80$ %, $T = 723$ K, WHSV = 4 h^{-1}).

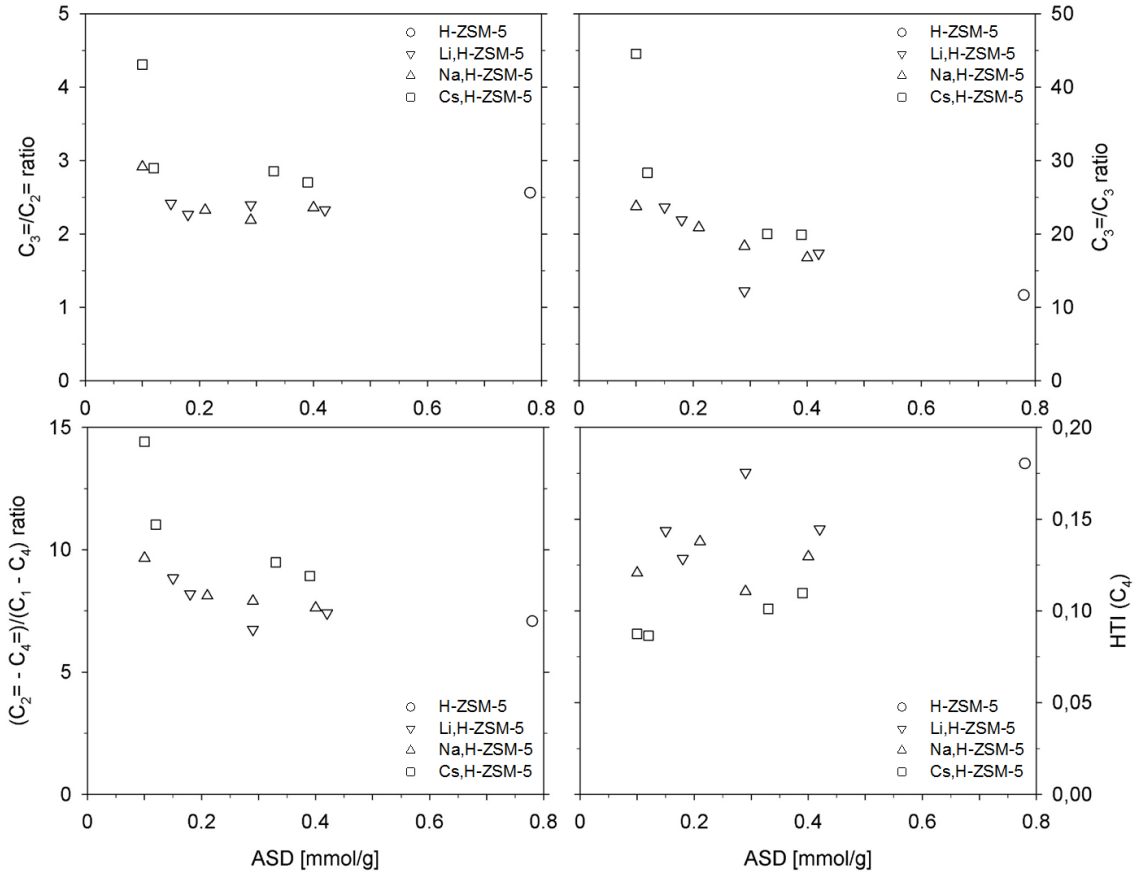

Figure S15: Physicochemical descriptors of the MTO conversion as a function of the acid site density (ASD) of the parent H-ZSM-5 and modified Li,H-; Na,H-; and Cs,H-ZSM-5 catalysts. From left top to bottom right: propene/ethene ratio ($C_3=/C_2=$), propene/propane ratio ($C_3=/C_3$), alkene/alkane ratio of the C_1-C_4 fraction ($C_2= - C_4=)/(C_1 - C_4)$), and hydrogen transfer index (HTI) of all C_4 products ($X \approx 80$ %, $T = 723$ K, WHSV = 4 h^{-1}).