Electronic Supplementary Information

Engineering of ZSM-5 zeolite crystals for enhanced lifetime in the production of light olefins *via* 2-methyl-2-butene cracking

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Table S1. Average product selectivity evidenced over the zeolite catalysts during a single catalytic cycle in the conversion of methanol to olefins. Conditions: $T = 723$ K, $P = 1$ bar, $WHSV = 6\ g_{MeOH}\ g_{zeolite}^{-1}\ h^{-1}$.

Sample	Lifetime[a] (h)	$S_{C2=}$[b] (Cmol%)	$S_{C3=}$[b] (Cmol%)	$S_{C4=}$[b] (Cmol%)	STY[c] ($g_{C2-4=}\ g_{zeolite}^{-1}\ h^{-1}$)	$S_{C1-3alk}$[b] (Cmol%)	$S_{C4-7alk}$[b] (Cmol%)	S_{C6-8ar}[b] (Cmol%)
OH-M	18	10	27	17	3.28	5	32	10
OH-M-H	39	14	25	9	2.64	4	31	9
OH-N	27	8	20	12	2.38	7	36	15
OH-N-H	54	8	20	10	2.25	4	37	10
F-M	19	10	21	12	2.59	6	26	15
F-N	25	9	22	13	2.64	4	27	13
F-N-H	42	7	24	11	2.49	3	33	9

[a] Time on stream during which X_{MeOH}>80%. [b] Selectivity to ethene ($S_{C2=}$), propene ($S_{C3=}$), butenes ($S_{C4=}$), light alkanes ($S_{C1-3alk}$), gasoline-range alkanes ($S_{C4-7alk}$), and to benzene, toluene, and xylene aromatics (S_{C6-8ar}). [c] Space-time yield of C2-4 olefins.

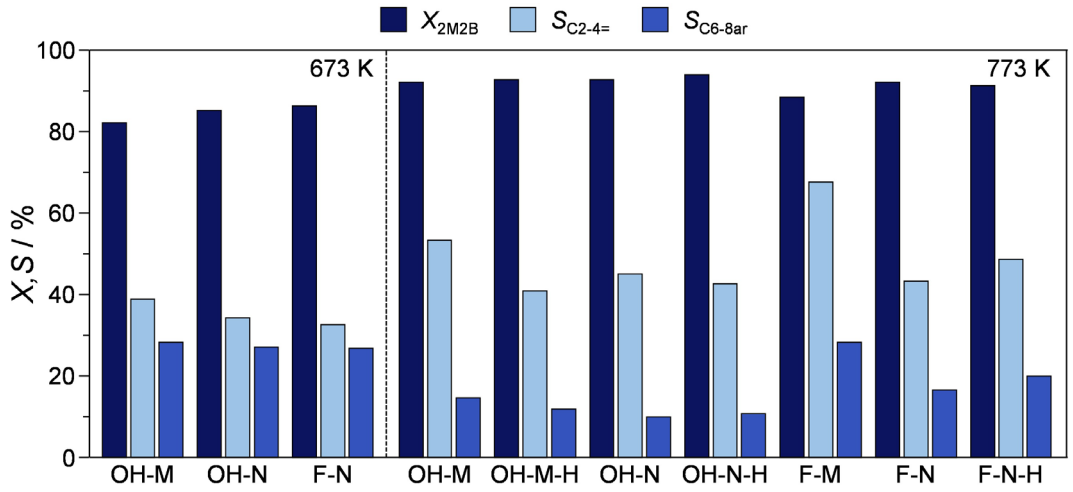

Figure S1. Conversion and selectivity over selected ZSM-5 catalysts in 2M2B cracking at different temperatures. Conditions: $t = 2$ h, $P = 1$ bar, $WHSV = 12$ g_{2M2B} h^{-1} $g_{catalyst}^{-1}$.

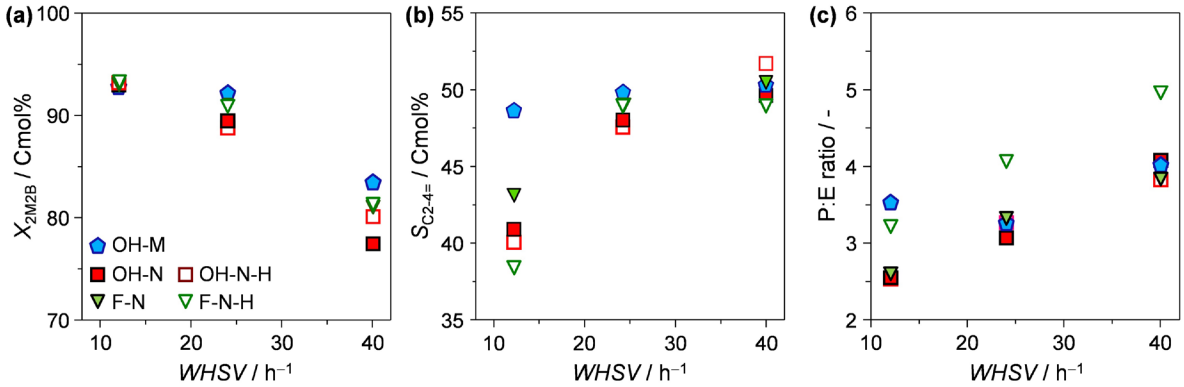

Figure S2. (a) Conversion, (b) olefin selectivity, and (c) the propylene:ethylene ratio in 2M2B cracking over selected ZSM-5 catalysts *versus* the weight hourly space velocity. Conditions: $t = 2$ h, $T = 773$ K, $P = 1$ bar.

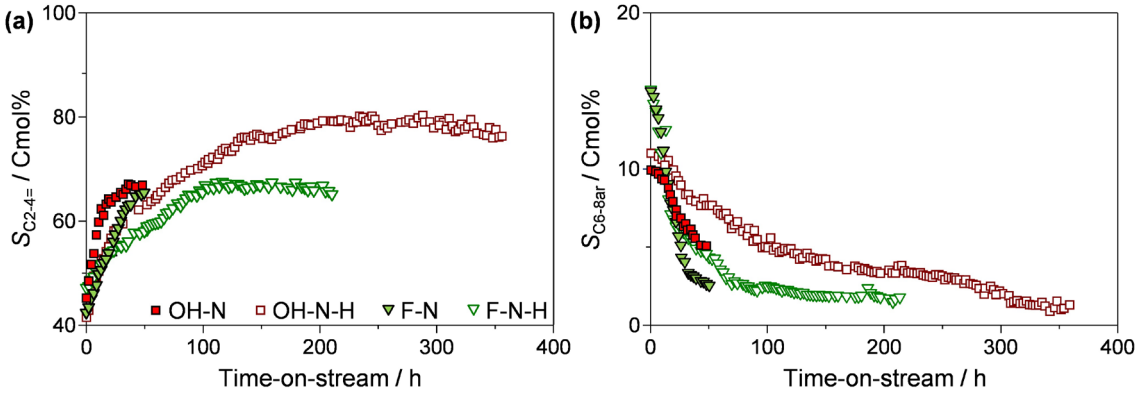

Figure S3. Selectivity to (a) light olefins ($S_{C2-4=}$) or (b) aromatics (S_{C6-8ar}) *versus* time-on-stream in 2M2B cracking over the nanosized zeolites and their desilicated analogues. Conditions: $T = 773$ K, $P = 1$ bar, $WHSV = 12\ g_{2M2B}\ g_{zeolite}^{-1}\ h^{-1}$.

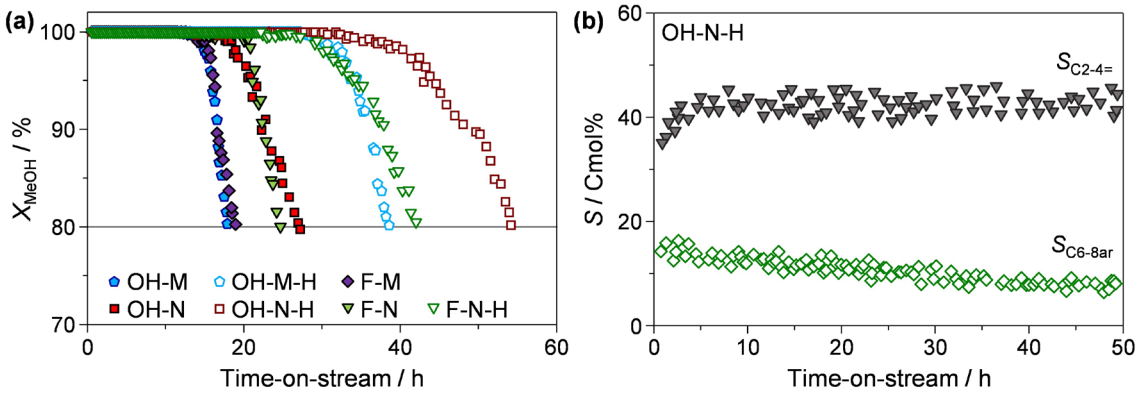

Figure S4. (a) Conversion and (b) selectivity to light olefins ($S_{C2-4=}$) or aromatics (S_{C6-8ar}) *versus* time-on-stream in the conversion of methanol to olefins over the ZSM-5 zeolites studied. The grey line indicates the degree of conversion at which a single catalytic cycle was defined. Conditions: $T = 723$ K, $P = 1$ bar, $WHSV = 6\ g_{MeOH}\ g_{zeolite}^{-1}\ h^{-1}$.