Supporting information for

Proximity-Guided Control of Framework Al Pairs in ZSM-5 for Enhancing Hydride Transfer and Aromatics Formation in Propane-DME Co-aromatization

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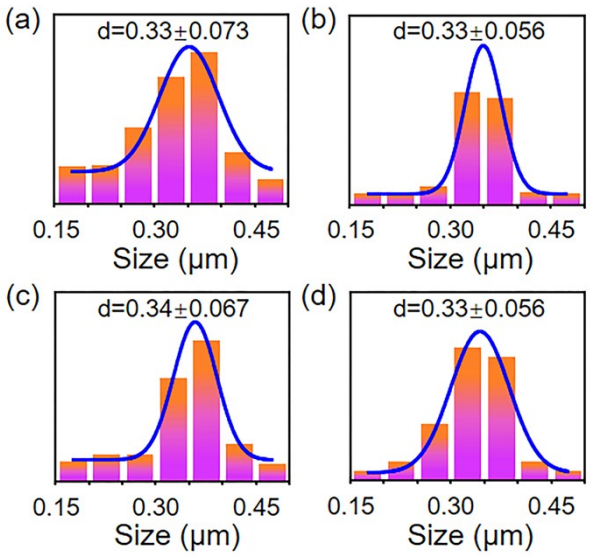

Fig. S1. Particle size distribution of (a) H-Z5-50, (b) H-Z5 -62, (c) H-Z5-78, (d) H-Z5-54. The average particle size is also labelled.

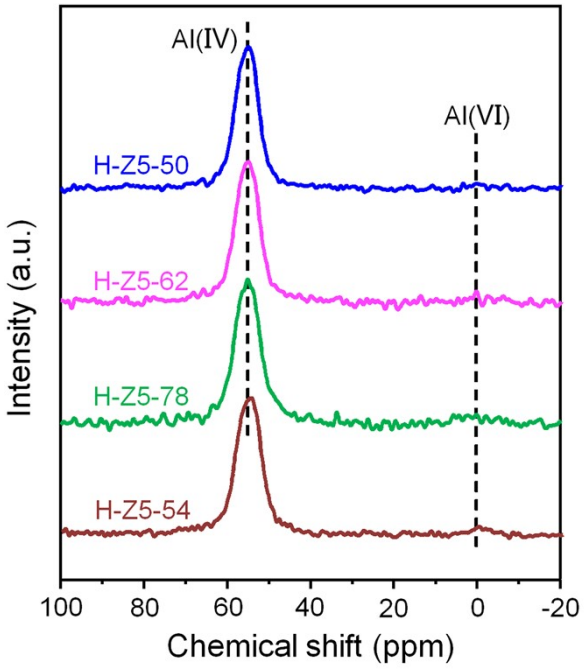

Fig. S2. Solid state ^{27}Al MAS NMR spectra of the HZSM-5 zeolites with varying Al-pair fractions.

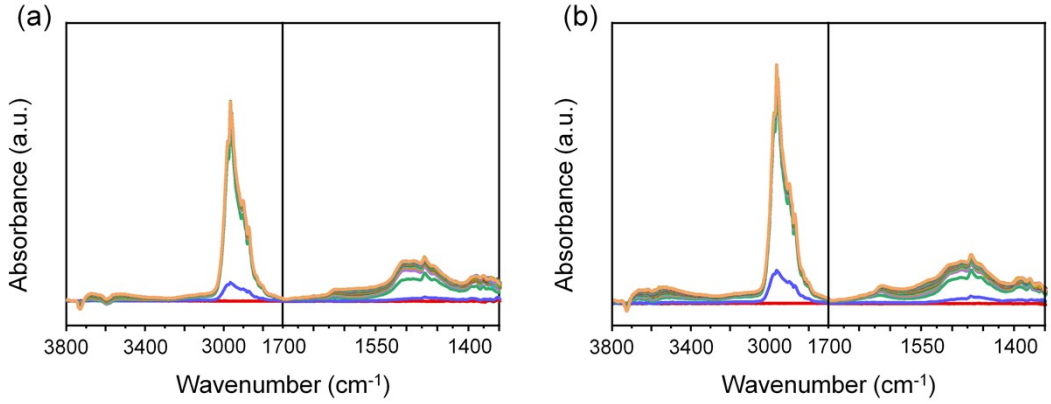

Fig. S3. Development of FTIR spectra for H-Z5-50 (a) and H-Z5-78 (b) at 400 °C depending on TOS for the co-aromatization of propane and DME.

Table S1. The conversion of propane and the distribution of products over the HZSM-5 catalysts during sole propane aromatization and the co-aromatization of propane and DME.

Sole propane aromatization						
Catalysts	Conversion of C_3H_8 (%)	Selectivity (%)				
		$C_1 + C_2$	$C^=$	C_4	$C_5 + C_6$	Aromatics
H-Z5-50	2.6	26.6	34.5	36.5	2.4	
H-Z5-62	3.4	25.1	31.7	40.7	2.5	-
H-Z5-78	3.7	24.2	24.3	48.9	2.6	-
H-Z5-54	2.8	25.5	29.7	42.3	2.5	-
Co-aromatization of propane and DME						
Catalysts	Conversion of C_3H_8 (%)	Selectivity (%)				
		$C_1 + C_2$	$C^=$	C_4	$C_5 + C_6$	Aromatics
H-Z5-50	3.3	10.2	21.6	53.9	2.5	11.8
H-Z5-62	4.1	10.9	18.1	56.0	2.4	12.6
H-Z5-78	4.8	12.5	16.2	56.1	2.2	13.0
H-Z5-54	3.7	11.4	19.3	54.6	2.4	12.3

Reaction conditions: 400 °C, 1 bar, WHSV = 0.9 h^{-1}, C-mol% of DME in the co-feedstock = 5 %.

Table S2. The conversion of propane and the distribution of products over the HZ-SH-2 and HZ-SH-6 at different temperature during sole propane aromatization and the co-aromatization of propane and DME.

Sole propane aromatization							
Temp (°C)	Catalysts	Conversion of C_3H_8 (%)	Selectivity (%)				
			$C_1 + C_2$	$C^=$	C_4	$C_5 + C_6$	Aromatics
400	H-Z5-50	2.6	26.6	34.5	36.5	2.4	-
	H-Z5-78	3.7	24.2	24.3	48.9	2.6	-
450	H-Z5-50	8.1	28.9	34.5	31.4	1.5	3.7
	H-Z5-78	11.4	28.8	24.4	35.2	1.6	10.0
500	H-Z5-50	22.4	34.7	32.3	13.9	0.9	18.2
	H-Z5-78	30.5	37.2	24.0	14.5	0.6	23.7
Co-aromatization of propane and DME							
Temp (°C)	Catalysts	Conversion of C_3H_8 (%)	Selectivity (%)				
			$C_1 + C_2$	$C^=$	C_4	$C_5 + C_6$	Aromatics
400	H-Z5-50	3.3	10.2	21.6	53.9	2.5	11.8
	H-Z5-78	4.8	12.5	16.2	56.1	2.2	13.0
450	H-Z5-50	9.6	23.7	30.2	34.8	2.0	9.3
	H-Z5-78	13.2	26.5	23.3	35.4	1.5	13.3
500	H-Z5-50	24.4	33.4	31.0	16.1	0.9	18.6
	H-Z5-78	31.9	36.4	23.2	14.8	0.6	25.0

Reaction conditions: 1 bar, WHSV = 0.9 h^{-1}, C-mol% of DME in the co-feedstock = 5 %.

Table S3. Characteristic IR frequencies of OH groups and carbenium ions vibration assignment.

Frequency (cm^{-1})	Assignment
3728	ν(OH) Si-OH terminal
3601	ν(OH) SiOHAl of framework Al
2967	$\nu_{asym}(CH_2)$ Saturated oligomeric carbenium ions
2902	ν_{asym} (CH_3)
2872	$\nu_{sym}(CH_2)$
2889	$\nu_{sym}(CH_3)$
1632	π-adsorbed C_3H_8 to SiOHAl
1618	π-adsorbed C_2H_4 to SiOHAl
1608	Aromatic carbenium ions
1586	dienyl carbenium ions
1538	Poly- or cyclic-enyl carbenium ions
1505	Mono-enyl carbenium ions
1440-1486	$\delta(CH_2)$ and $\delta(CH_3)$

Table S4. The activation free energy barrier (G_a) and reaction free energy (ΔG_r) for the hydrogen transfer and chain growth reactions mediated by $ZOCH_3$ on single Al and Al pairs (in eV).

	single Al		Al pairs	
	G_a	ΔG_r	G_a	ΔG_r
$ZOCH_3 + C_3H_8 \rightarrow ZOH + C_3H_6 + CH_4$	0.86	-0.33	0.70	-0.28
$ZOCH_3 + C_3H_6 \rightarrow ZO^- + C_4H_9^+$	0.55	0.12	0.48	-0.06
$ZO^- + C_3H_8 + C_4H_9^+ \rightarrow ZOC_3H_7 + C_4H_{10}$	0.44	-0.14	0.28	-0.37

Table S5. Computed energy contributions for hydrogen transfer and chain growth processes at 773K.

Hydrogen transfer:

Isolated Al H-ZSM-5						
	E	△ZPE	△ZPE-T△S	E+△ZPE	E+△ZPE-T△S	G(773K)
1	-2386.38	3.82	2.65	-2382.56	-2383.74	-0.03
2	-2385.26	3.65	2.39	-2381.61	-2382.88	0.83
3	-2385.35	3.65	2.16	-2381.70	-2383.19	0.51
4	-2386.19	3.66	2.13	-2382.53	-2384.06	-0.36
Paired Al H-ZSM-5						
	E	△ZPE	△ZPE-T△S	E+△ZPE	E+△ZPE-T△S	G(773K)
1	-2388.02	3.82	2.60	-2384.20	-2385.42	-0.12
2	-2387.06	3.66	2.35	-2383.40	-2384.72	0.58
3	-2386.96	3.65	2.07	-2383.31	-2384.89	0.41
4	-2387.84	3.67	2.14	-2384.17	-2385.69	-0.40

Chain growth:

Isolated Al H-ZSM-5						
	E	△ZPE	△ZPE-T△S	E+△ZPE	E+△ZPE-T△S	G(773K)
5	-2377.96	3.18	2.05	-2374.78	-2375.92	-0.05
6	-2377.21	3.14	1.85	-2374.07	-2375.36	0.50
7	-2377.93	3.17	2.14	-2374.77	-2375.79	0.07
8	-2436.01	5.96	4.02	-2430.05	-2431.99	-1.03
9	-2435.48	5.94	3.93	-2429.54	-2431.55	-0.59
10	-2436.42	6.13	4.29	-2430.29	-2432.13	-1.17
Paired Al H-ZSM-5						
	E	△ZPE	△ZPE-T△S	E+△ZPE	E+△ZPE-T△S	G(773K)
5	-2379.59	3.18	2.03	-2376.41	-2377.56	-0.10
6	-2379.08	3.15	2.01	-2375.93	-2377.08	0.38
7	-2379.59	3.17	1.97	-2376.42	-2377.62	-0.16
8	-2437.67	5.96	3.99	-2431.72	-2433.68	-1.13
9	-2437.31	5.94	3.91	-2431.37	-2433.40	-0.85
10	-2438.12	6.12	4.32	-2431.99	-2433.80	-1.25

1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 denote the corresponding elementary steps $ZOCH_3$ +C_3H_8, TS, ZO^-+$C_3H_7^+$+CH_4, ZOH+C_3H_6+CH_4, ZOH+C_3H_6, TS1, ZO^-+$C_4H_9^+$+CH_4, ZO^-+ C_3H_8+ $C_4H_9^+$, TS2 and ZOC_3H_7+C_4H_{10}, respectively.