Electronic supplementary material

Boosting propane dehydroaromatization by confining PtZn alloy nanoparticles within H-ZSM-5 crystals

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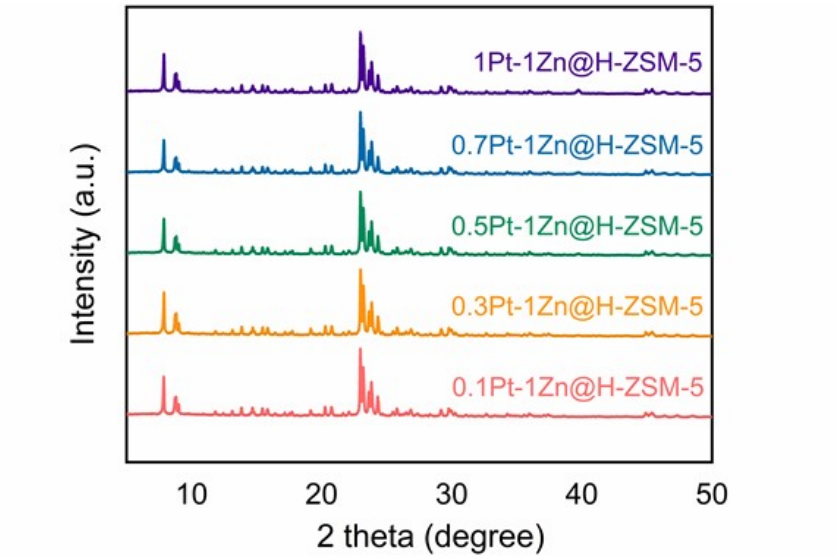

Fig. S1. XRD patterns of bifunctional *x*Pt-1Zn@H-ZSM-5 catalysts

Table S1 Textural properties of H-ZSM-5, *y*Zn@H-ZSM-5, and *x*Pt-*y*Zn @H-ZSM-5 catalysts.

Catalyst	Si/Al [a] ratio	S_{BET} [b] ($m^2\ g^{-1}$)	S_{micro} [c] ($m^2\ g^{-1}$)	V_{total} [d] ($cm^3\ g^{-1}$)	V_{micro} [e] ($cm^3\ g^{-1}$)	Crystal sizes [f] (μm)
H-ZSM-5	15	363	253	0.20	0.11	1–2
H-ZSM-5	35	354	252	0.18	0.10	1–2
H-ZSM-5	60	353	267	0.23	0.11	1–2
H-ZSM-5	120	314	262	0.24	0.10	1–2
0.5Zn@H-ZSM-5	15	338	244	0.19	0.11	1–2
1Zn@H-ZSM-5	15	338	246	0.19	0.11	1–2
2Zn@H-ZSM-5	15	328	246	0.19	0.11	1–2
3Zn@H-ZSM-5	15	308	239	0.17	0.11	1–2
4Zn@H-ZSM-5	15	303	233	0.17	0.10	1–2
5Zn@H-ZSM-5	15	275	214	0.16	0.10	1–2
0.7Pt@H-ZSM-5	15	323	236	0.20	0.10	1–2
0.7Pt-1Zn@H-ZSM-5	15	313	228	0.18	0.10	1–2

[a] By X-ray fluorescence spectrometry

[b] BET method

[c] t-plot method

[d] Single point desorption total pore volume, $P/P_0 = 0.99$

[e] t-plot method

[f] By scanning electron microscopic (SEM)

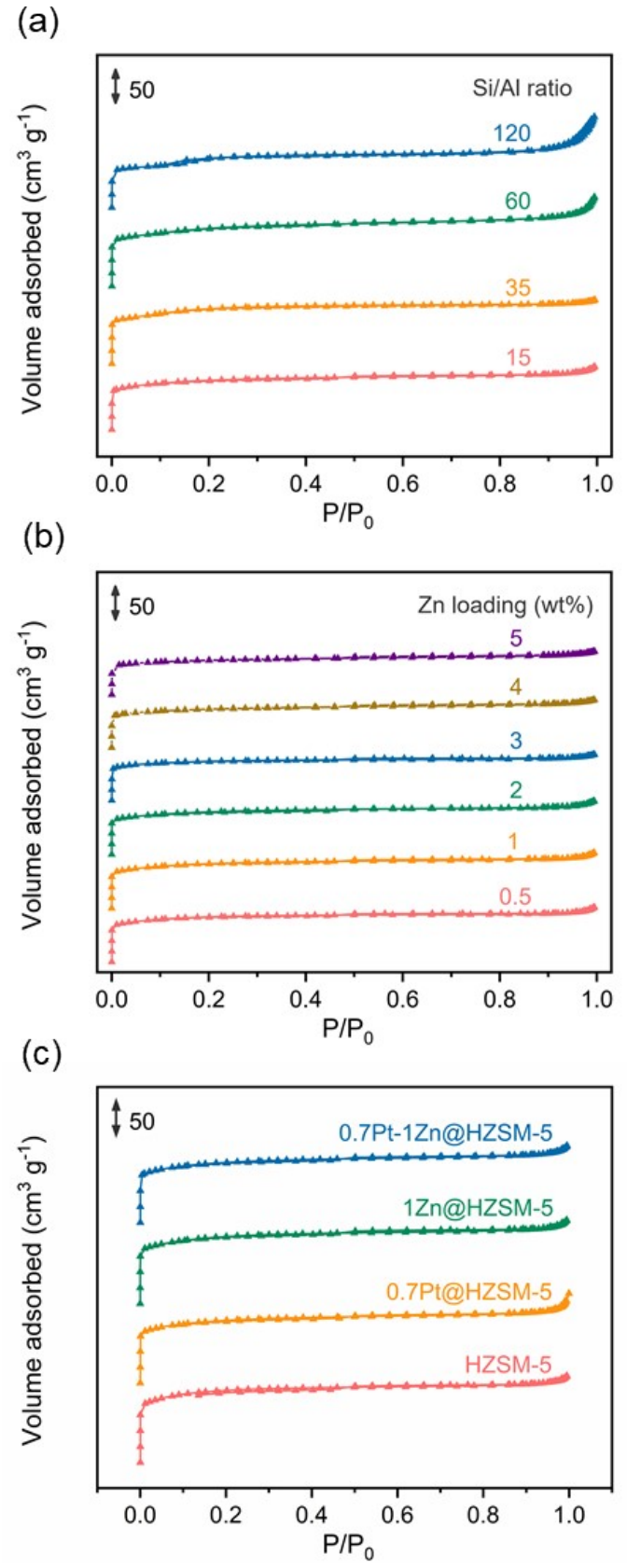

Fig. S2. N_2 adsorption-desorption isotherms of (a) H-ZSM-5 with different Si/Al ratios, (b) *y*Zn@H-ZSM-5, and (c) 0.7Pt-1Zn@H-ZSM-5.

Table S2 Acid densities of catalysts estimated by NH_3-TPD and Pyridine-adsorbed FT-IR.

Catalyst	Si/Al ratio	Acidity by NH_3-TPD (μmol g^{-1})[a]			Acidity by Py-FTIR (μmol g^{-1})		
		Strong	weak	total	Brønsted	Lewis	B/L
H-ZSM-5	15	357	567	924	237	11	21
H-ZSM-5	35	159	224	383	132	12	11
H-ZSM-5	60	90	124	214	61	19	3
H-ZSM-5	120	51	70	121	29	12	2
0.5Zn@H-ZSM-5	15	319	590	909	218	50	4.4
1Zn@H-ZSM-5	15	295	562	857	206	109	1.9
2Zn@H-ZSM-5	15	217	504	721	114	160	0.7
3Zn@H-ZSM-5	15	182	551	733	81	145	0.6
4Zn@H-ZSM-5	15	157	559	716	80	189	0.4
5Zn@H-ZSM-5	15	139	532	671	70	205	0.3
0.7Pt@H-ZSM-5	15	342	558	900	223	33	6.8
0.7Pt-1Zn@H-ZSM-5	15	311	563	874	213	86	2.5

[a] By deconvolution of NH_3-TPD profiles

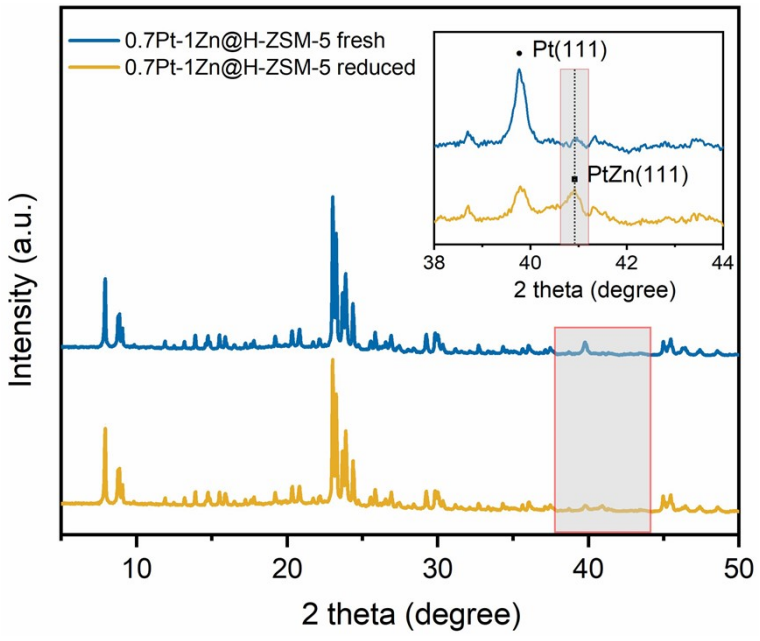

Fig. S3. XRD profiles for 0.7Pt-1Zn@H-ZSM-5 before and after reduction by H_2 at 550 °C for 2 h.

Table S3 Catalytic performances of 1Ga/H-ZSM-5 and *x*Pt-1Zn@H-ZSM-5 catalysts.

Catalyst	C_3H_8 conv. (%)	Selectivity(%)						Aro. yield (%)
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_{4+}	Aro.	
1Ga/H-ZSM-5	40	17.6	8.4	8.9	8.3	4.0	53	21
Ga@H-ZSM-5	31	11	7.4	20	15	4.6	42	13
1Zn@H-ZSM-5	34	14	8.7	9.7	9.6	2.9	55	19
0.7Pt@H-ZSM-5	81	8.4	1.9	45	6.1	1.9	36	30
0.05Pt-1Zn@H-ZSM-5	39	12	7	12.7	10	2.3	56	22
0.1Pt-1Zn@H-ZSM-5	68	5.0	1.0	30	9.2	2.8	53	36
0.3Pt-1Zn@H-ZSM-5	71	4.8	0.9	30	8.9	2.6	53	38
0.5Pt-1Zn@H-ZSM-5	72	4.7	0.8	30	8.9	2.4	53	38
0.7Pt-1Zn@H-ZSM-5	72	4.6	0.8	30	8.7	2.4	54	39
1.0Pt-1Zn@H-ZSM-5	72	4.5	0.8	31	8.9	2.4	52	38

Reaction condition: W_{cat} = 0.2 g, F_{C3H8} = 10 mL min^{-1}, F_{N2} = 10 mL min^{-1}, T = 550 °C, P = 1 bar, TOS = 10 min.

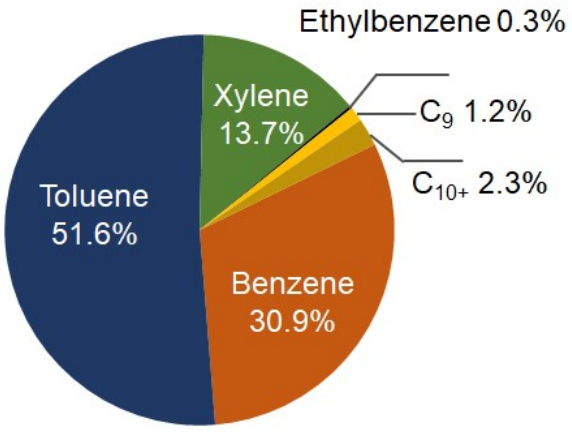

Fig. S4. Distribution of aromatic hydrocarbons over 0.7Pt-1Zn@H-ZSM-5. Reaction condition: W_{cat} = 0.2 g, F_{C3H8} = 10 mL min^{-1}, F_{N2} = 10 mL min^{-1}, T = 550 °C, P = 1 bar, TOS = 10 min.

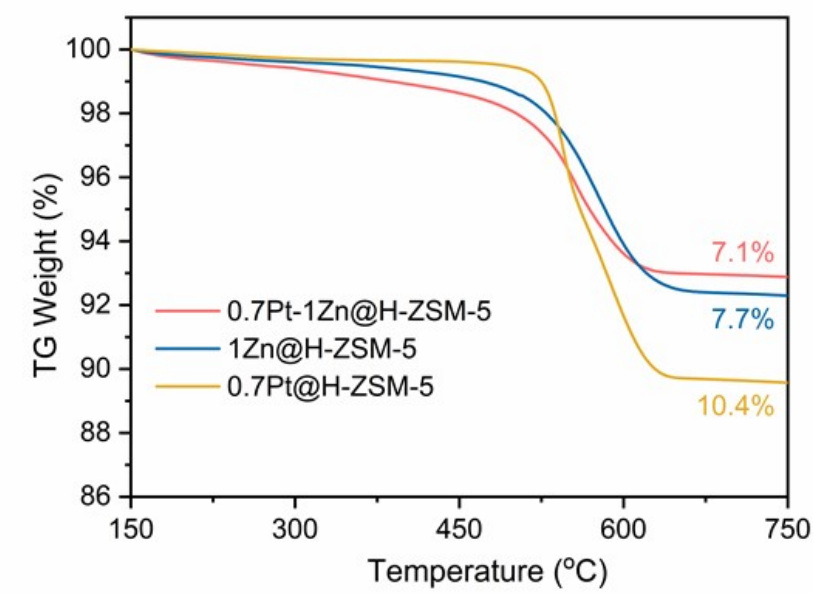

Fig. S5. TG analysis of 0.7Pt@H-ZSM-5, 1Zn@H-ZSM-5, and 0.7Pt-1Zn@H-ZSM-5 catalysts after reaction for 10 h. Compared with converted propane, about 0.2% of propane in weight percentage was converted into coke.

Table S4 Textural properties of 1Zn@H-ZSM-5, 0.7Pt@H-ZSM-5, and 0.7Pt-1Zn@H-ZSM-5 catalysts after reaction for 10 h.

Catalyst	Si/Al [a] atomic ratio	S_{BET} [b] ($m^2\ g^{-1}$)	S_{micro} [c] ($m^2\ g^{-1}$)	V_{total} [d] ($cm^3\ g^{-1}$)	V_{micro} [e] ($cm^3\ g^{-1}$)
1Zn@H-ZSM-5	15	338	246	0.19	0.11
1Zn@H-ZSM-5-10 h	15	117	84	0.08	0.04
0.7Pt@H-ZSM-5	15	323	236	0.20	0.10
0.7Pt@H-ZSM-5-10 h	15	34	23	0.01	0.01
0.7Pt-1Zn@H-ZSM-5	15	313	228	0.18	0.10
0.7Pt-1Zn@H-ZSM-5-10 h	15	103	80	0.07	0.04

[a] By X-ray fluorescence spectrometry

[b] BET method

[c] t-plot method

[d] Single point desorption total pore volume, $P/P_0 = 0.99$

[e] t-plot method

Table S5 Acid densities of 1Zn@H-ZSM-5, 0.7Pt@H-ZSM-5, and 0.7Pt-1Zn@H-ZSM-5 catalysts after reaction for 10 h.

Catalyst	Si/Al ratio	Acidity by NH_3-TPD (μmol g^{-1})[a]		
		Strong	weak	total
1Zn@H-ZSM-5	15	295	562	857
1Zn@H-ZSM-5-10 h	15	156	375	531
0.7Pt@H-ZSM-5	15	342	558	900
0.7Pt@H-ZSM-5-10 h	15	30	126	156
0.7Pt-1Zn@H-ZSM-5	15	311	563	874
0.7Pt-1Zn@H-ZSM-5-10 h	15	167	362	529

[a] By deconvolution of NH_3-TPD profiles

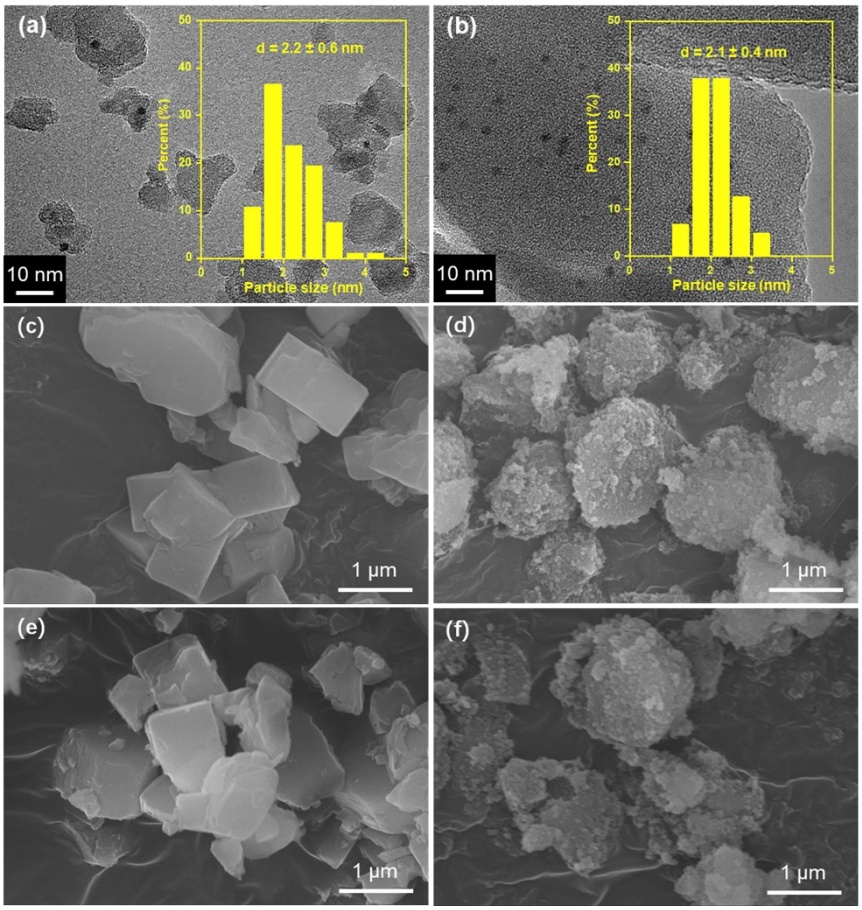

Fig. S6. TEM images of (a) 0.7Pt-1Zn/Al_2O_3 and (b) 0.7Pt-1Zn@H-ZSM-5, the insets show the Pt-Zn nanoparticle size distribution. SEM images of (c) H-ZSM-5, (d) 0.7Pt-1Zn/Al_2O_3/H-ZSM-5, (e) 0.7Pt-1Zn@H-ZSM-5, and (f) 0.7Pt-1Zn@H-ZSM-5/Al_2O_3.

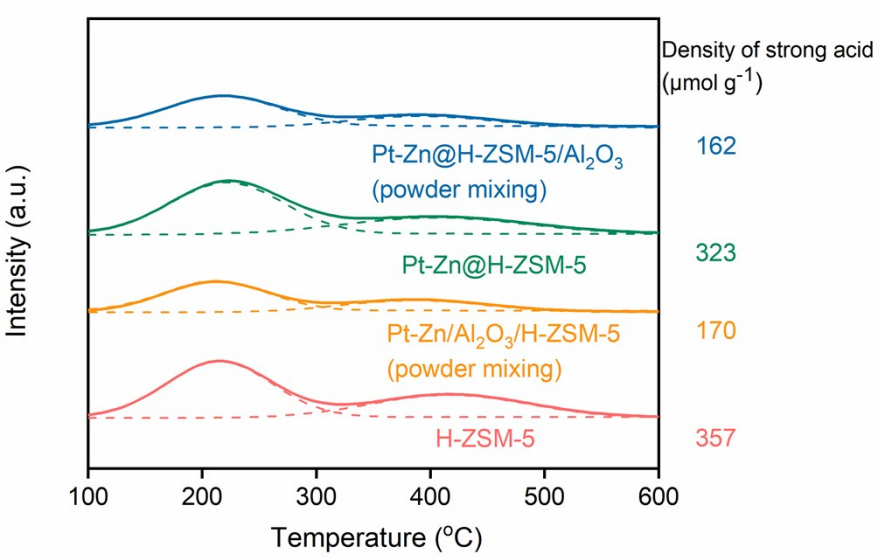

Fig. S7. NH_3-TPD profiles of different samples. The density of strong acid evaluated from the high-temperature peak was normalized to zeolite weight and displayed in the figure.

Table S6 Pt loading and Zn loading of samples.

Samples	Pt loading (wt%)[a]	Zn loading (wt%)[a]
Pt-Zn/Al_2O_3	0.69	1.15
Pt-Zn/Al_2O_3/H-ZSM-5	0.32	0.61
Pt-Zn@H-ZSM-5	0.74	1.13
Pt-Zn@H-ZSM-5/Al_2O_3	0.35	0.58

[a] By inductive coupled plasma-atomic emission spectrometer (ICP-AES)

Table S7 The effect of contact time over catalysts with different spatial distances between functional sites.

Spatial distance	Contact time (s)	C_3H_8 conv. (%)	Selectivity (%)						Aro. yield (%)
			CH_4	C_2H_4	C_2H_6	C_3H_6	C_{4+}	Aro.	
millimeter scale	1.2	42	24	13	14	11	6.4	32	13
micrometer scale	1.2	41	20	12	14	8.8	3.6	42	17
nanometer scale	1.2	42	15	8.1	16	8.2	2.7	50	21
atom scale	1.2	74	4.7	0.7	29	7.5	2.0	56	41
millimeter scale	2.4	45	27	14	16	10	8.0	25	11
micrometer scale	2.4	46	25	13	19	8.8	3.2	31	14
nanometer scale	2.4	44	16	7.6	22	8.3	3.1	43	19
atom scale	2.4	81	5.8	0.8	32	5.5	1.5	55	45

Reaction condition: $W_{(cat)}$ = 0.4 g, $F_{(C3H8)}$ = 10 or 5 mL min^{-1}, $F_{(N2)}$ = 10 or 5 mL min^{-1}, T = 550 °C, P = 1 bar, TOS = 10 min.