Tailored Ga-modified zeolites for efficient chemical recycling of polyolefins into aromatics

Qing HE [a, b], Oğuzhan AKIN [a], Parviz YAZDANI [a], Rengui WENG [b], Devanshu SAJWAN [c], Lingfeng LI [a], Mozhdeh AMANATI [a], Robin J. VARGHESE [a], Kevin M. VAN GEEM [a, *]

[a] Laboratory for Chemical Technology (LCT), Department of Materials, Textiles and Chemical Engineering, Faculty of Engineering and Architecture, Ghent University, Technologiepark-Zwijnaarde 125, Zwijnaarde 9052, Oost-Vlaanderen, Belgium

[b] Institute of Biology and Chemistry, Fujian University of Technology, No. 69 Xuefu South Road, Fuzhou 350108, Fujian, China

[c] Inorganic Chemistry and Catalysis, Institute for Sustainable and Circular Chemistry, Department of Chemistry, Utrecht University, Universiteitsweg 993584 CG, Utrecht, The Netherlands

Supporting information

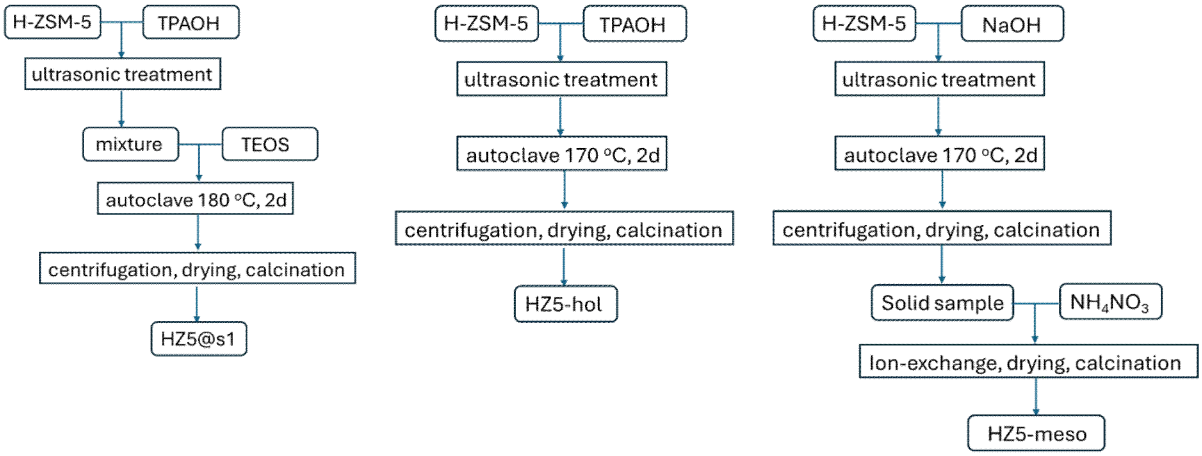

Figure S1 Schematic diagram of the modified HZ5 preparation process

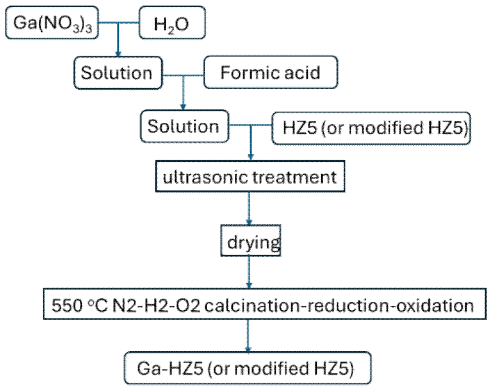

Figure S2 Schematic diagram of the preparation of Ga-loaded zeolite catalysts

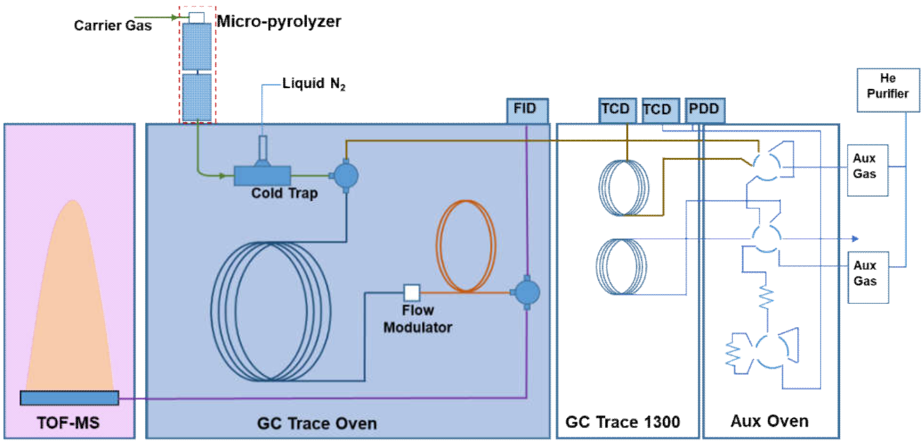

Figure S3 Schematic diagram of experimental apparatus

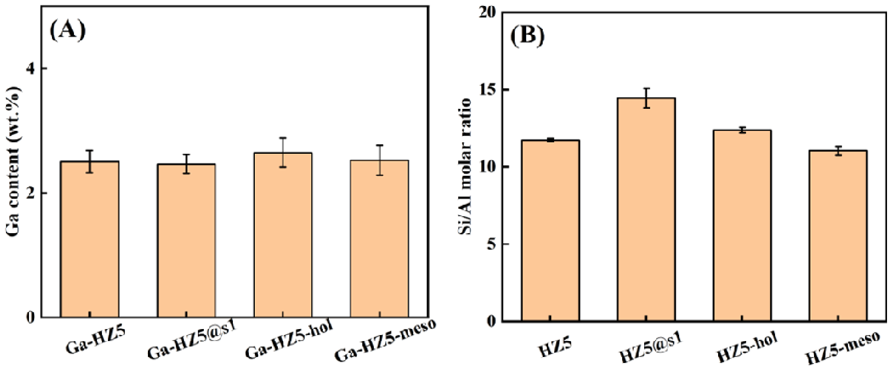

Figure S4 EDX results of different catalysts (A) Ga content (B) Si/Al ratio

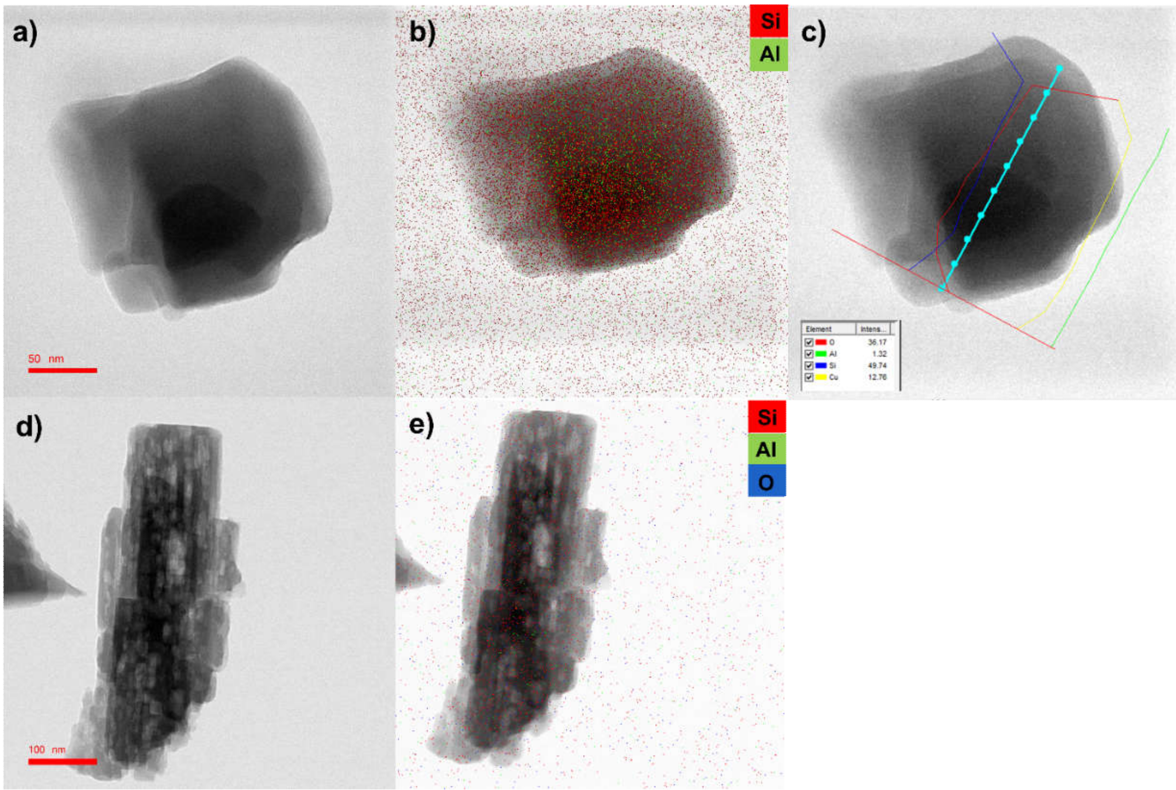

Figure S5 TEM images of HZ5-based catalysts showing different structural features after post-synthesis modification

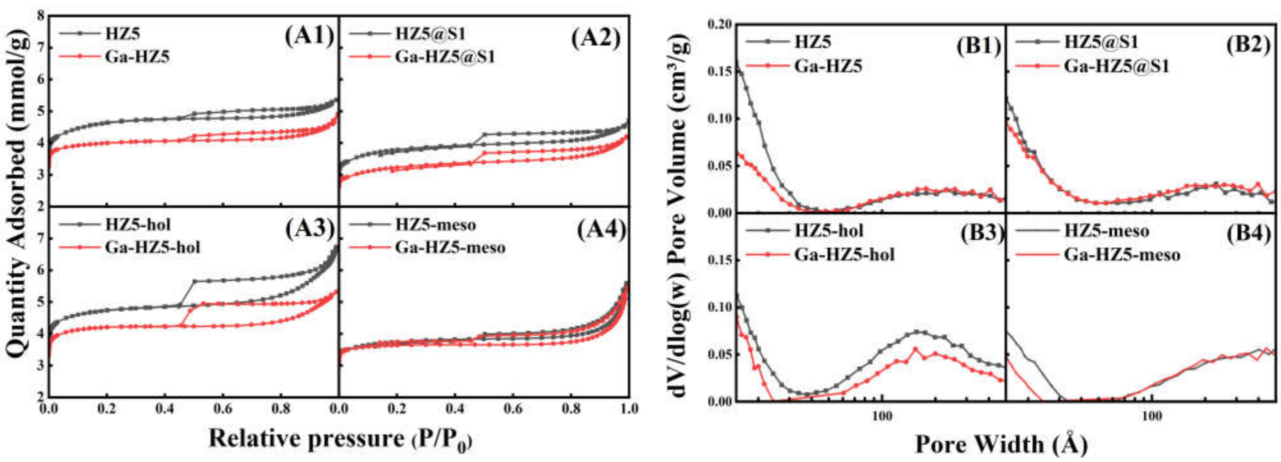

Figure S6 (A) N_2 adsorption/desorption isotherms (B) Pore size distribution of catalysts (BJH adsorption branch)

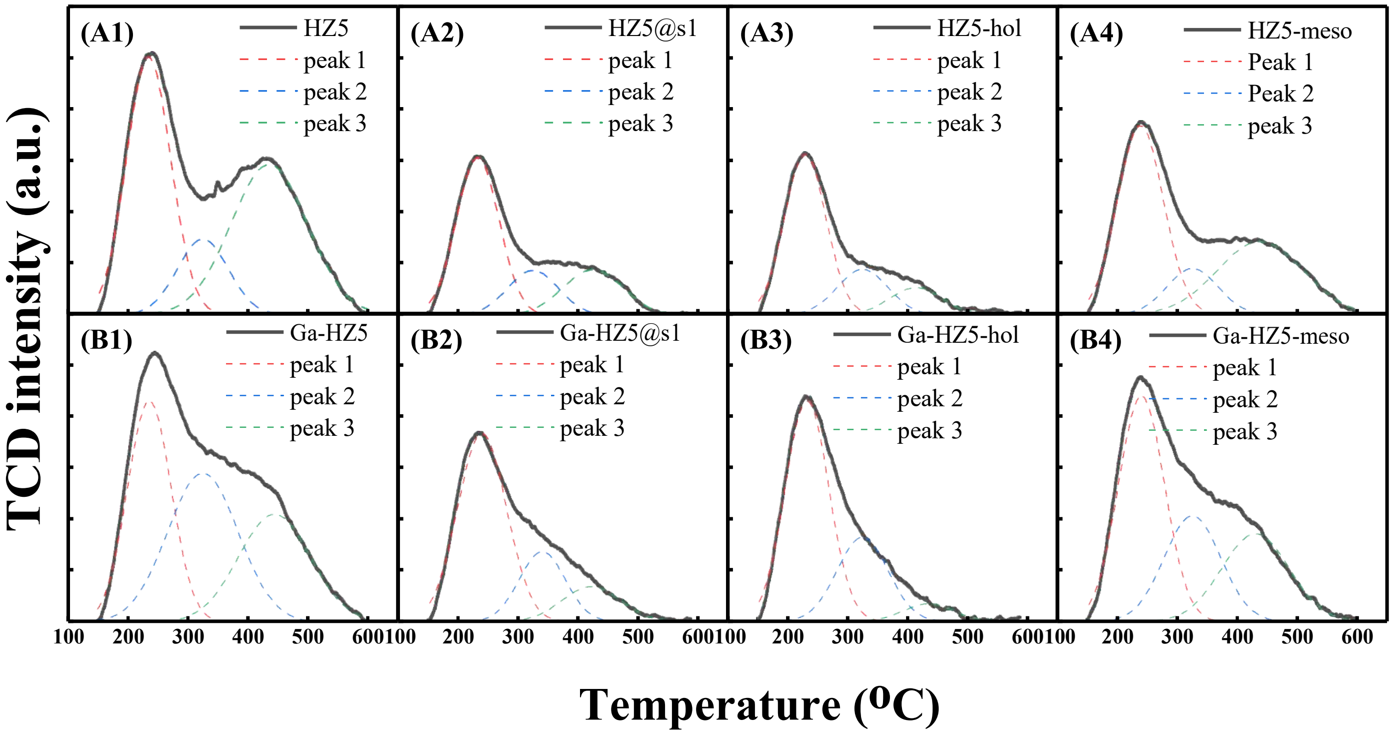

Figure S7 Peak deconvolution analysis of NH_3-TPD profiles for catalysts (A) without Ga loading and (B) with Ga loading.

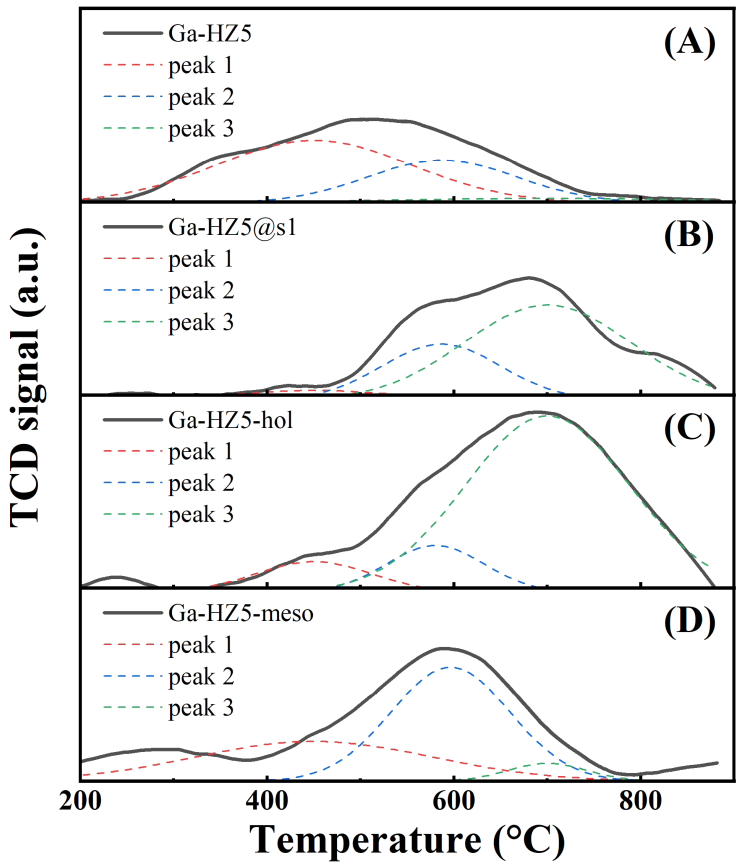

Figure S8 Peak deconvolution analysis of H_2-TPR for different catalysts

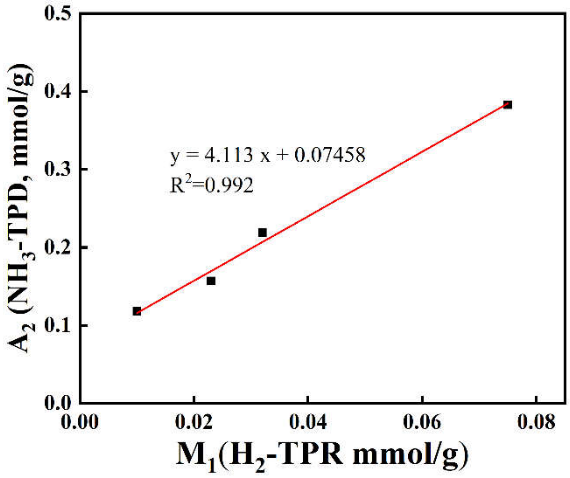

Figure S9 Relationship between H_2 consumption and medium acid sites

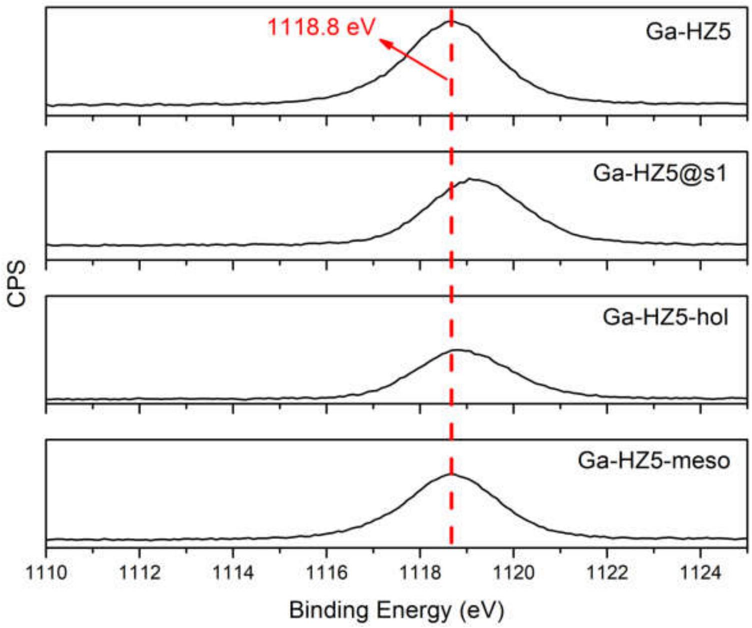

Figure S10 The Ga $2p_{3/2}$ spectra of Ga-modified catalysts

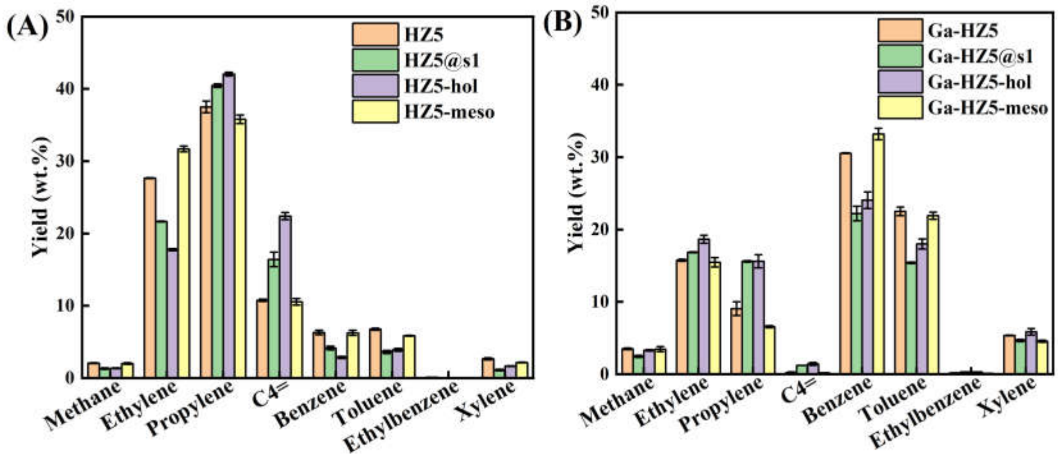

Figure S11 Main product yields of PP catalytic pyrolysis (A) Ga-free zeolite (B) Ga-loaded zeolite

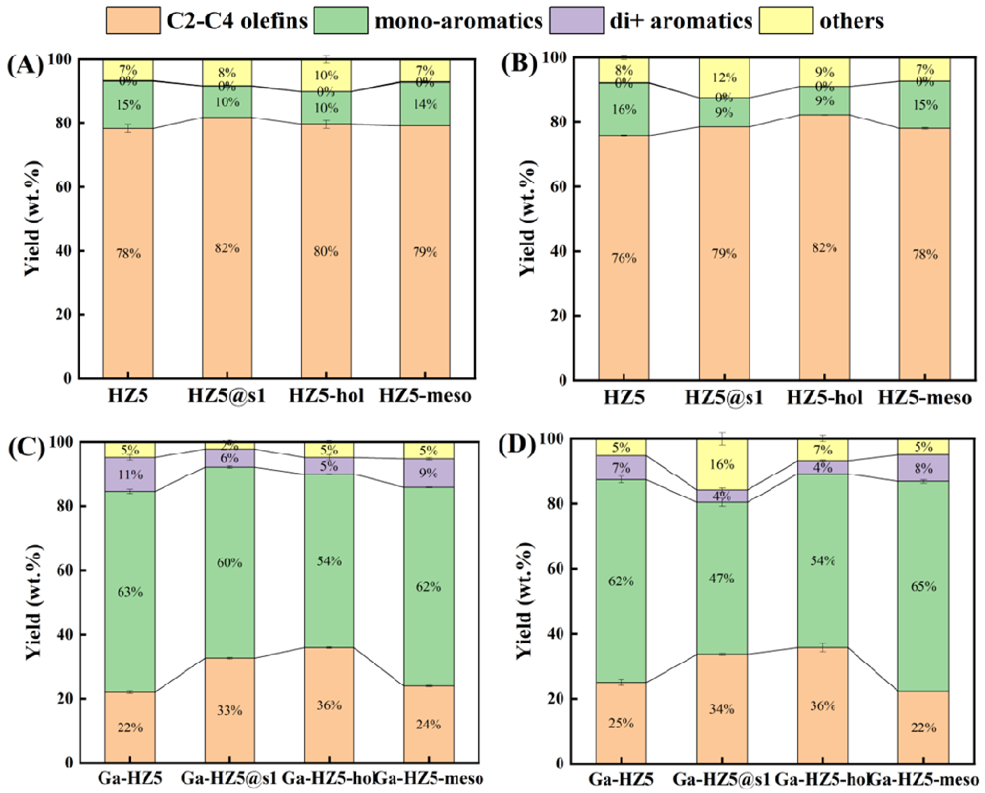

Figure S12 Group yields of catalytic pyrolysis (A) LDPE over Ga-free zeolite (B) PP over Ga-free zeolite (C) LDPE over Ga-loaded zeolite (D) PP over Ga- loaded zeolite

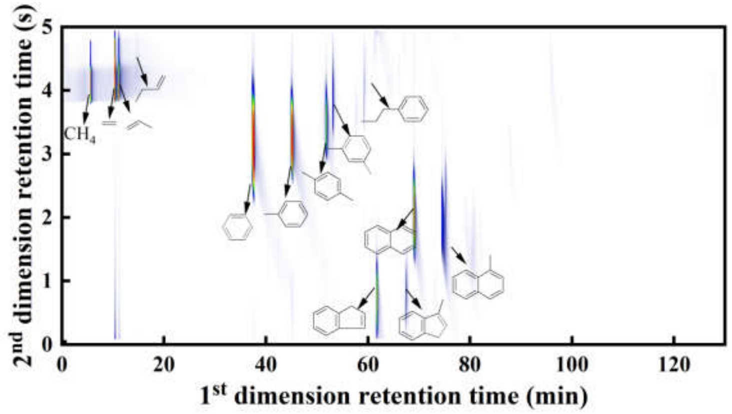

Figure S13 Product distribution of LDPE over Ga-HZ5

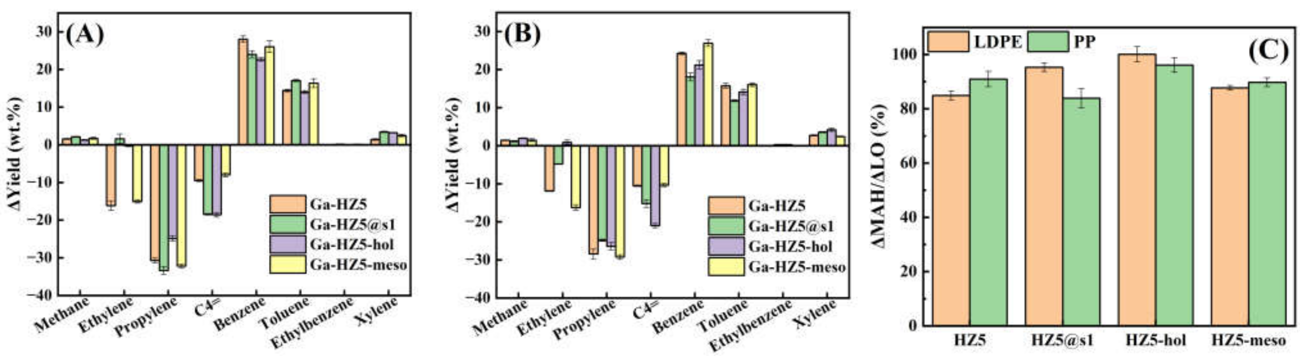

Figure S14 Comparison of main product yields before and after Ga loading for (A) LDPE and (B) PP pyrolysis, and (C) variations in the ΔMA/ΔLO ratio induced by Ga loading over different catalysts.

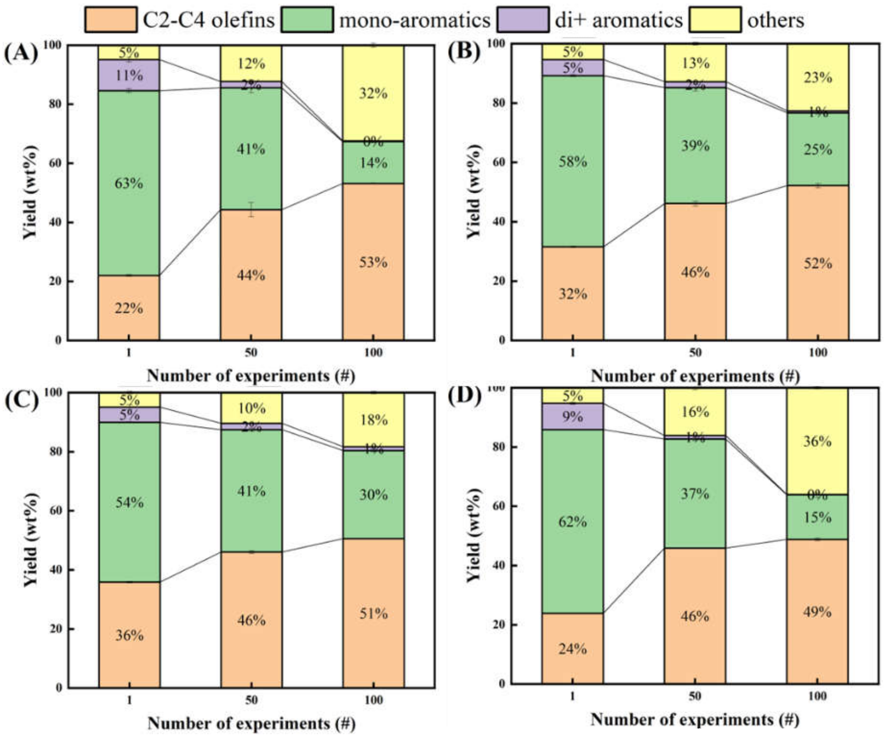

Figure S15 Evolution of grouped product yields with increasing experimental runs LDPE as feedstock (A) Ga-HZ5 (B) Ga-HZ5@s1 (C) Ga-HZ5-hol (D) Ga-HZ5-meso

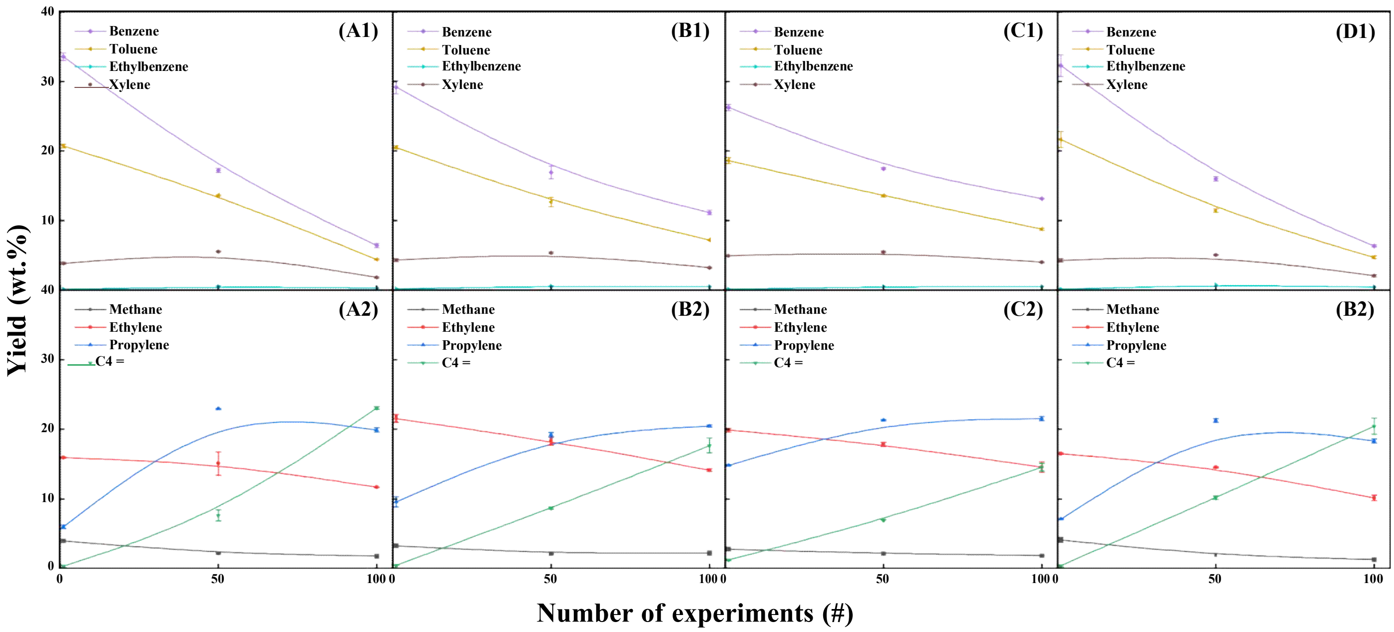

Figure S16 Evolution of main product yields with increasing experimental runs (A) Ga-HZ5 (B) Ga-HZ5@s1 (C) Ga-HZ5-hol (D) Ga-HZ5-meso

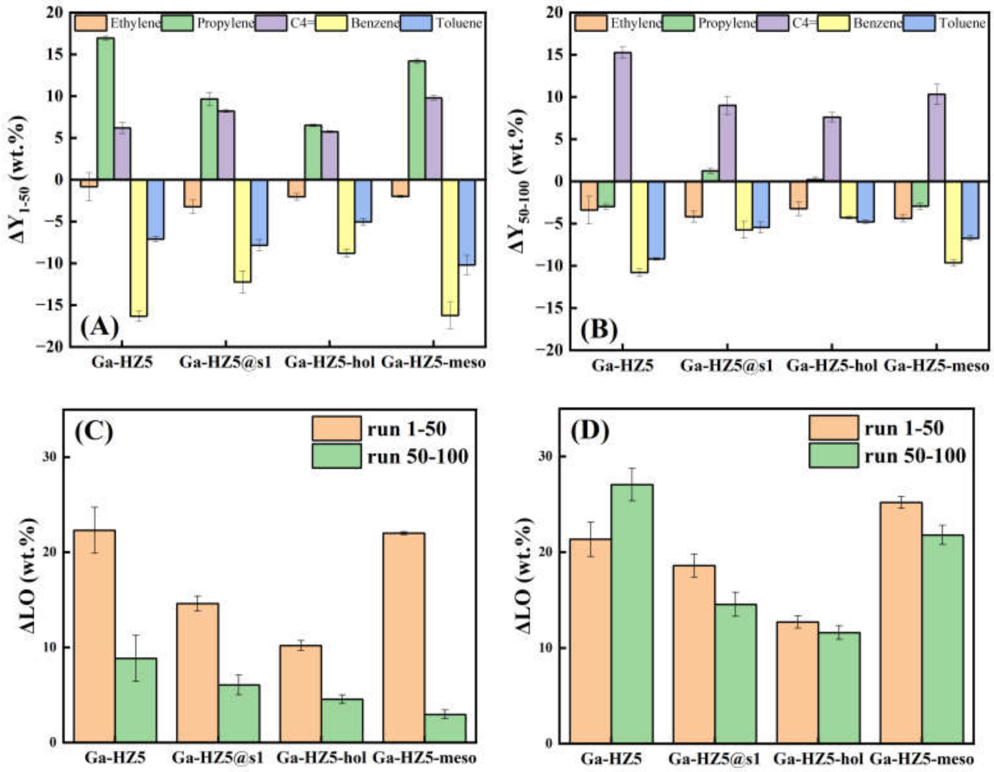

Figure S17 Changes in product yields over different catalysts with increasing experimental runs: (A) main product yields during runs 1-50, (B) main product yields during runs 50-100, (C) LO group yield, and (D) MAH group yield.

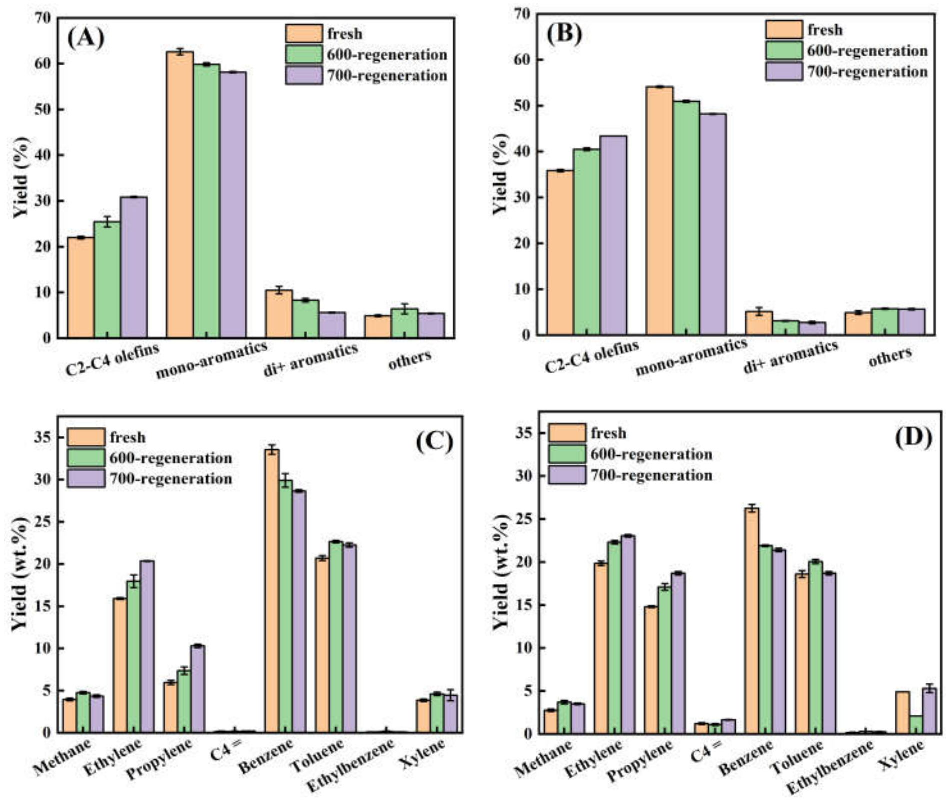

Figure S18 Product distributions of regenerated catalysts, including grouped product distributions for (A) Ga-HZ5 and (B) Ga-HZ5-hol, and corresponding main product distributions for (C) Ga-HZ5 and (D) Ga-HZ5-hol.

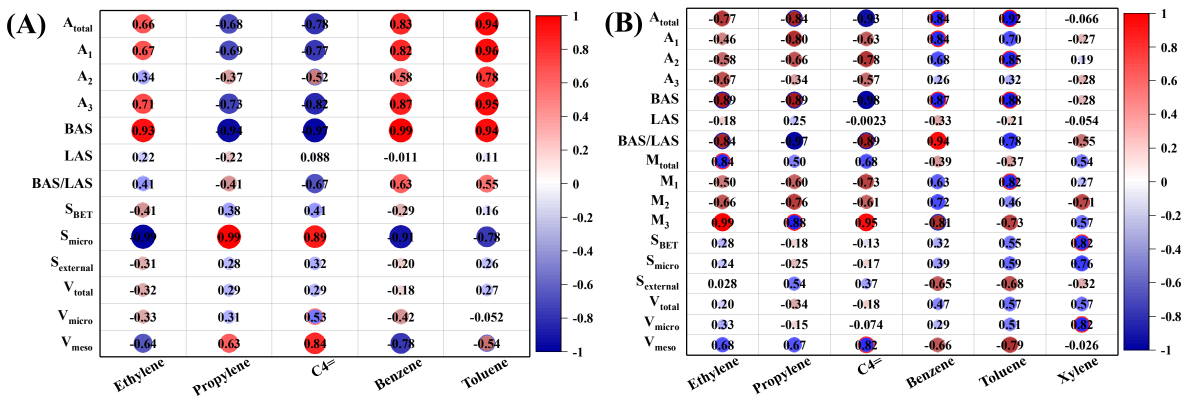

Figure S19 Correlation between PP catalytic pyrolysis product and catalyst structure (A) Ga-free catalyst (B) Ga-loaded catalyst

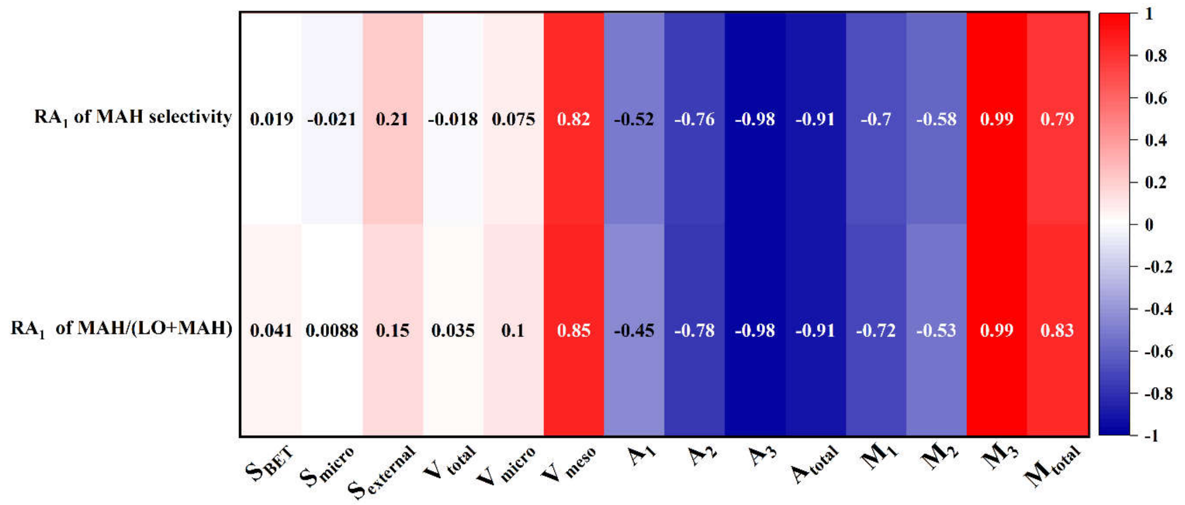

Figure S20 Correlation of catalyst structure and stability RA_1 (at 100 run)

Table S1 Brief summary of literature on the catalytic pyrolysis of polyolefins over Ga-HZSM5 in two-stage reactors

No.	Parent HZSM Si/Al	Catalyst preparation	Feedstock	catalyst/plastic ratio	Reaction conditions	Product distribution(wt.%) *	Ref.
1	25	11 wt.%	PE/PP	NA/0.2 mg	600 °C He 30 mL/min	H_2: NA C_2-C_4: 11.1 MAH: 76.9	[1]
2	11.5	3 wt.%	LDPE/PP	8 mg/0.4 mg	600 °C He 50 mL/min	H_2: 2.0; C_2-C_4: 22; MAH: 63	This work
3	12.5	1 wt % Ga; TPAOH treatment	HDPE	0.35 g/1 g	500 °C	H_2: 2.2; C_2-C_4: 10; MAH: 60	[2]
4	12.5	3 wt % Ga; with $(NH_4)_2HPO_4$	LDPE	4 g/ 10 g	500-550 °C	H_2: 2.2 C_2-C_4: 50.6 MAH: 46.2	[3]
5	12.5	3 wt % Ga NaOH treatment,	LDPE	6 g/ 8 g	500-550 °C, CO_2 100 mL/min	H_2: 2.6 C_2-C_4: 32 MAH: 46	[4]
6	25	1 wt % Ga	LDPE	8 mg/0.4 mg	600 °C, He 20 mL/min	H_2: NA C_2-C_4:37; MAH: 44	[5]
7	30	1 wt % Ga, reduction-oxidation	pp	2 g/6 g	600-550 °C, CH_4/N_2/He 50 mL/min	H_2: 1.2 C_2-C_4:35 MAH: 39.5	[6]
8	12.5	7 wt.%; NaOH treatment	LLDPE	NA/7g	550 °C, N_2 100 mL/min	H_2: 4.8 C_2-C_4: 31 MAH: 32	[7]

*: maximum MAH value reported in related literature. Data converted to mass fractions based on reported gas/liquid/solid yields and selectivity.

Table S2 Catalytic pyrolysis product distribution over Ga-free catalysts

Component	HZ5		HZ5@s1		HZ5-hol		HZ5-meso	
	LDPE	PP	LDPE	PP	LDPE	PP	LDPE	PP
H_2	0.29±0.01	0.32±0.01	0.20±0.03	0.16±0.01	0.21±0.01	0.16±0.01	0.29±0.01	0.29±0.01
methane	2.41±0.04	2.05±0.12	1.16±0.08	1.30±0.11	1.48±0.01	1.36±0.09	2.37±0.29	1.99±0.11
C_2-C_4 olefins	78.19±1.40	76.14±0.89	82.09±1.51	78.32±1.71	80.10±1.66	81.89±0.52	79.11±0.41	77.94±0.67
C_2-C_4 alkanes	1.86±0.07	1.89±0.67	2.23±0.26	1.40±0.23	1.70±0.02	0.94±0.06	1.83±0.34	1.80±0.22
BTX	14.36±0.49	15.85±0.00	9.55±0.44	8.84±0.77	9.93±0.02	8.44±0.57	13.29±0.35	14.27±0.47
C_9+ alkyl aromatics	0.27±0.06	0.33±0.00	0.26±0.01	0.22±0.12	0.44±0.06	0.36±0.07	0.23±0.03	0.20±0.00
C_5+ aliphatics	2.44±0.19	3.89±0.19	4.98±0.41	9.74±0.25	6.82±1.70	6.61±0.22	2.81±0.19	3.46±0.31
PAHs	0.18±0.02	0.17±0.02	0.08±0.02	0.09±0.02	0.09±0.01	0.10±0.02	0.30±0.14	0.07±0.03

Table S3 Catalytic pyrolysis product distribution over Ga-loaded catalysts

Component	Ga-HZ5	Ga-HZ5@s1	Ga-HZ5-hol	Ga-HZ5-meso

	LDPE	PP	LDPE	PP	LDPE	PP	LDPE	PP
H_2	1.26±0.03	1.29±0.05	1.14±0.03	0.92±0.05	1.10±0.01	1.06±0.02	1.26±0.01	1.33±0.03
methane	3.97±0.21	3.52±0.14	3.25±0.15	2.47±0.21	2.74±0.25	3.30±0.13	4.14±0.25	3.44±0.48
C_2-C_4 olefins	21.94±0.53	25.03±1.34	31.54±0.26	33.74±0.25	35.82±0.45	35.64±1.82	23.99±0.43	22.17±0.54
C_2-C_4 alkanes	0.14±0.05	0.19±0.07	0.29±0.03	0.46±0.10	0.56±0.18	0.40±0.01	0.21±0.11	0.14±0.05
BTX	58.16±1.43	58.44±1.08	54.15±0.66	42.64±1.06	49.91±1.17	48.13±0.04	58.27±0.17	59.76±0.52
C_9+ alkyl aromatics	4.29±0.10	4.04±0.27	3.47±0.07	4.17±0.21	4.16±0.67	5.46±0.00	4.02±0.70	4.78±0.65
C_5+ aliphatics	0.75±0.09	1.57±0.17	1.77±0.03	12.87±2.78	1.59±0.45	3.21±1.43	1.00±0.39	1.42±0.28
PAHs	10.48±1.09	7.33±0.06	5.47±0.04	3.80±0.88	5.15±1.17	3.94±0.36	8.90±0.39	8.17±0.13

References

[1] D. Guo, Z. Cai, Y. Ye, A. Kumar, H. Rong, B. Cui, and M. Hu, J. Energy. Inst., **2026**, 125, 102443

[2] K. Qian, W. Tian, S. Yan, W. Li, L. Yin, D. Guo, Z. Yang, D. Chen, and Y. Feng, Fuel, **2024**, 357, 129781

[3] J. Zhang, M. Ma, Z. Chen, X. Zhang, H. Yang, X. Wang, H. Feng, J. Yu, and S. Gao, J. Energy. Inst., **2023**, 108, 101235

[4] J. Zhang, D. Lai, Z. Chen, X. Wang, Q. Xiong, J. Li, X. Zhang, B. O. Oboirien, and G. Xu, ACS Sustainable Chem. Eng., **2024**, 12, 13137-13148

[5] O. Akin, Q. He, M. Havaei, F. D. Calik, D. Withoeck, R. J. Varghese, P. Yazdani, P. Van Steenberge, and K. M. Van Geem, Catal. Today, **2025**, 459, 115429

[6] H. Shim, S. Pyo, A. Kumar, Y. Khani, S. Q. Choi, K. Cho, J. Lee, and Y.-K. Park, Chinese Journal of Catalysis, **2025**, 73, 368-383

[7] L. Fu, H. Lin, L. Zhu, Q. Wang, H. Luo, Q. Xiong, V. S. Vladimirovich, and Y. Zhou, J. Anal. Appl. Pyrol., **2023**, 175, 106186