Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

The synergistic interplay of hierarchy, crystal size, and Ga-promotion in the methanol-to-aromatics process over ZSM-5 zeolites

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S1. Materials and Methods

S1.1 Chemicals

Tetraethyl orthosilicate (TEOS, 99wt%, Shanghai Macklin, China), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, 99.9 wt%, Shanghai Macklin, China), sodium hydroxide (NaOH, 99.9wt%, Sinopharm Chemical Reagent, China), tetrapropyl-ammonium hydroxide (TPAOH, 40 wt% or 25 wt% in H_2O, HEOWNS, China), gallium nitrate ($Ga(NO_3)_3$, 99.9 wt%, Shanghai Macklin, China), glucose ($C_6H_{12}O_6$, AR, Shanghai Macklin, China), and deionized water (≥ 18.25 MΩ·cm under 25 °C) were used as received unless stated otherwise.

S1.2 Preparation of Zeolite Materials

Preparation of ZSM-5 (m-ns) and Ga/ZSM-5 (m-ns) zeolites:

The synthesis scheme of microporous ZSM-5 zeolite referred to the literature, including the Mintova group[1] and our previous work. [2,3] In general, the ZSM-5 precursor suspension composition was the following: $1SiO_2$: 0.4TPAOH: $0.004Al_2O_3$: $12H_2O$. Typically, the Al precursor and deionized water were added to a small beaker and stirred for 15 minutes. It was followed by the dropwise addition of TPAOH (40% in water) as an organic structure directing agent (OSDA) and stirring of the resultant solution for 30 minutes. Next, TEOS was added dropwise, and the synthesis gel was

magnetically stirred at 800 rpm for 12 hours. Then, the aged precursor suspension was transferred into a 50 mL Teflon-lined autoclave. It is then subjected to hydrothermal treatment at 150 °C for 72 hours under autogenous pressure in a static oven. The collected solid was separated and purified by high-speed centrifugation (12,000 rpm) after repetitive washing with deionized water until the pH value was less than 8. The sample was dried at 80 °C for 8 h and calcined at 550 °C for 5 h. This as-synthesized zeolite was noted as “ZSM-5 (m-ns)”.

Utilizing $Ga(NO_3)_3$ as the gallium salt precursor, 2 wt% Ga was introduced into the parent ZSM-5 (m-ns) zeolite via impregnation. Post-impregnation, the sample was dried at 100°C and subsequently calcined at 550 °C for 5 hours. This sample was designated “Ga/ZSM-5 (m-ms)” zeolite.

Preparation of ZSM-5 (h-hexag) and Ga/ZSM-5 (h-hexag) zeolites:

The synthesis protocol of hierarchical ZSM-5 zeolite with hexagonal prism shape was conceptually similar to the previous section, but with three following fundamental differences: (i) Glucose as the hard template led to the change in the crystal morphology of synthesized zeolites, (ii) use of 25% TPAOH as MFI-OSDA, and (iii) Si/H_2O ratio. During this synthesis, the composition of precursor suspension was the following: $1SiO_2$: 0.4TPAOH: $0.004Al_2O_3$: 0.1glucose: $20H_2O$. Typically, the Al precursor and deionized water were added to a small beaker and stirred for 15

minutes. It was followed by the dropwise addition of TPAOH (25% in water) and mixing the resultant solution for 30 min. In the next step, the glucose was added to the above mixture and stirred for 30 min. Next, TEOS was added dropwise, and the synthesis gel was magnetically stirred at 800 rpm for 12 hours. The aged precursor suspension was transferred into a 50 mL Teflon-lined autoclave and subjected to hydrothermal treatment at 150 °C for 72 h under autogenous pressure in a static oven. The harvested solid was separated and purified by high-speed centrifugation (12,000 rpm) after repetitive washing with deionized water until the pH value was 7. The sample was dried at 80 °C for 8 h and calcined at 550 °C for 5 h. This as-synthesized zeolite was noted as “ZSM-5 (h-hexag)” zeolite.

Also utilizing $Ga(NO_3)_3$ as the gallium salt precursor, 2 wt % Ga has been introduced into the parent ZSM-5 (h-hexag) zeolite via impregnation. Post-impregnation, the sample was dried at 100°C and subsequently calcined at 550°C for 5 hours. This sample was designated as “Ga/ZSM-5 (h-hexag)” zeolite.

Preparation of ZSM-5 (h-coffin) and Ga/ZSM-5 (h-coffin) zeolite catalysts:

The synthesis method precisely followed the preparation of ZSM-5 (h-hexag) zeolite, solely altering (increasing) the dosage of glucose additives and Si/H_2O ratio to achieve the coffin-shaped hierarchical ZSM-5 zeolite. The composition of precursor suspension was the following: $1SiO_2$: 0.4TPAOH: $0.004Al_2O_3$: 0.2 glucose: $16H_2O$.

Typically, the Al precursor and deionized water were added to a small beaker and stirred for 15 minutes. It was followed by the dropwise addition of TPAOH (25% in water), and the resultant solution was stirred for 30 minutes. In the next step, the meso-OSDA glucose was added to the above mixture, and stirred for 30 min. Next, TEOS was added dropwise, and the synthesis gel was magnetically stirred at 800 rpm for 12 h. Afterward, the aged precursor suspension was transferred into a 50 mL Teflon-lined autoclave and subjected to hydrothermal treatment at 150 °C for 72 h under autogenous pressure in a static oven. The harvested solid was separated and purified by high-speed centrifugation (12,000 rpm) after repetitive washing with deionized water until the pH value was less than 8. The sample was then dried at 80 °C for 8 h and calcined at 550 °C for 5 h. This as-synthesized zeolite was noted as “ZSM-5 (h-coffin)” zeolite.

The exact same impregnation method was adopted for parent ZSM-5 (h-coffin) zeolite. The obtained sample was designated as “Ga/ZSM-5 (h-coffin)” zeolite.

S1.3 Catalysts Characterization

Powder X-ray diffraction (PXRD) patterns were acquired on Bruker D8 Advance X-ray diffractometer using Cu-Kα (1.54060 Å) radiation, and operated at 40 kV and 40 mA. In order to optimize the count statistics and peak shape profiles, data collection was carried out in the 2θ range of 5-60° using the step size of 0.01° and scan speed

of 5 deg/min and applying a low-angle cutting knife to avoid direct beam heating the detector [2,4,5]. The bulk chemical composition analysis was performed via inductively coupled plasma (ICP) measurements obtained in a 700 ICP-OES instrument (Agilent), where the samples were digested in acidic solutions under microwave treatment. X-ray fluorescence (XRF) measurements were obtained in a Shimadzu EDX-LE instrument. The high-resolution transmission electron microscopy (HR-TEM) imaging and elemental mapping were performed by Titan Themis-Z microscope (Thermo-Fisher Scientific). The crystal size distribution was determined by Nanomeasure software (developed by Fudan University, China). Ar physisorption was performed with an automated gas sorption system Micromeritics ASAP 2460 at -196 °C. The total specific surface area of all zeolite samples was determined using the BET method at low relative pressures. The total pore volume was determined at P/P_0 = 0.99, while the micropore volumes and micropore surface areas were evaluated using the t-plot method. Temperature-programmed NH_3 desorption (NH_3-TPD) was measured by BELCAT-B from Micky Bayer Co. Ltd (Japan). 50 mg of sample was used for the test in a 30 mL min^{-1} Ar flow. Prior to the test, the sample was heated to 550 °C and kept for 120 min to remove possible impurities. Afterward, the sample was cooled to 50 °C and exposed to a 30 mL min^{-1} NH_3 flow for 1 h to saturate the surface completely, which was followed by purging with a 30 mL min^{-1} ultrahigh purity He flows to remove any physically adsorbed NH_3 for 30 min. After all these pretreatments, the catalyst was heated from 50 ° to 600 °C at a rate of 10 °C min^{-1}. X-ray photoelectron spectra (XPS)

were recorded on a Thermo ESCALAB 250 XI spectrometer with Al Ka radiation (hv =1486.6 eV, 150 W,). The charge correction was performed using the adventitious carbon (C1s) peak at 284.8 eV.

S1.4 MTH Catalytic performance tests

Catalytic experiments for methanol-to-aromatics (MTA) were performed in a four-channel Flowrence®XD from Avantium. Prior to the reaction, zeolites were pelletized and crushed into 150-250 μm particles and the obtained catalysts (50 mg) were mixed with SiC (300 mg) at a weight ratio of 1:6 (catalyst/SiC) to avoid the formation of hot spots. [5,6] Then, the catalytic bed was pretreated with N_2 at 550 °C for 2 h. Reaction temperatures of 400 °C were tested and the WHSV value of methanol was 4 h^{-1}, diluting in N_2 to a constant molar MeOH:N_2 ratio of 1:4 at ambient pressure. The reaction products were analyzed on line by means of gas chromatography (GC) in an Agilent 7890B with three detectors: 2 FIDs and 1 TCD. The TCD channel has a PPQ as a backflush column, a Hayesep Q column for the separation of CO_2 and a Molsieve as an analytical column for the separation of He, H_2, N_2, CH_4 and CO. All other compounds (water, hydrocarbons and oxygenates) are backflushed. The FID is equipped with a 10-m precolumn with a wax stationary phase. The separation of C_1-C_5 hydrocarbons is carried out on a 30-m Gaspro stationary phase. And the separation of methanol and aromatics is carried out on a 30-m Wax stationary phase. Methanol

conversion (X, %) and selectivity (S, %) of each product are defined as follows:

$$X = \frac{n_{C,MeOH_{in}} - n_{C,MeOH_{out}} - 2 \cdot n_{C,DME_{out}}}{n_{C,MeOH_{in}}} \cdot 100\% \quad (1)$$

$$S_i = \frac{i \cdot n_{Ci}}{n_{C,MeOH_{in}} - n_{C,oxy_{out}}} \cdot 100\% \quad (2)$$

where CM_{eOHin} , $C_{MeOHout}$, CD_{MEout} and C_{oxyout} are the concentrations determined by GC analysis of methanol in the blank, and in the reactor effluent, respectively. A total selectivity to aromatics is calculated, including products such as benzene, toluene, (o-, m- and p-) xylenes (BTX) and all C_9-C_{10} aromatics. n_{ci} is the molar quantity of product *Ci* in the effluents and *i* is the number of carbon atoms in its molecule.

S2. Supplementary Figures

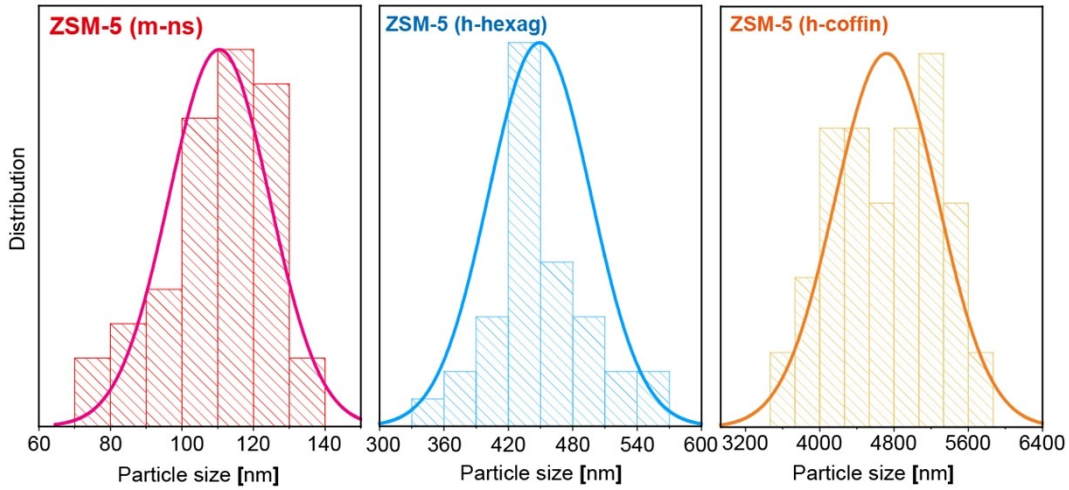

Fig. S1 Crystal size distribution of synthesized (from left-to-right) ZSM-5 (m-ns) with spherical shape and crystal size around 110 nm; ZSM-5 (h-hexag) with hexagonal bar-shape and crystal size around 450 nm, and ZSM-5 (h-coffin) zeolites with coffin-shape and crystal size around 4600 nm. The results were determined by Nanomeasure software based on the SEM images of corresponding zeolites (**Fig. 2(b-d)**).

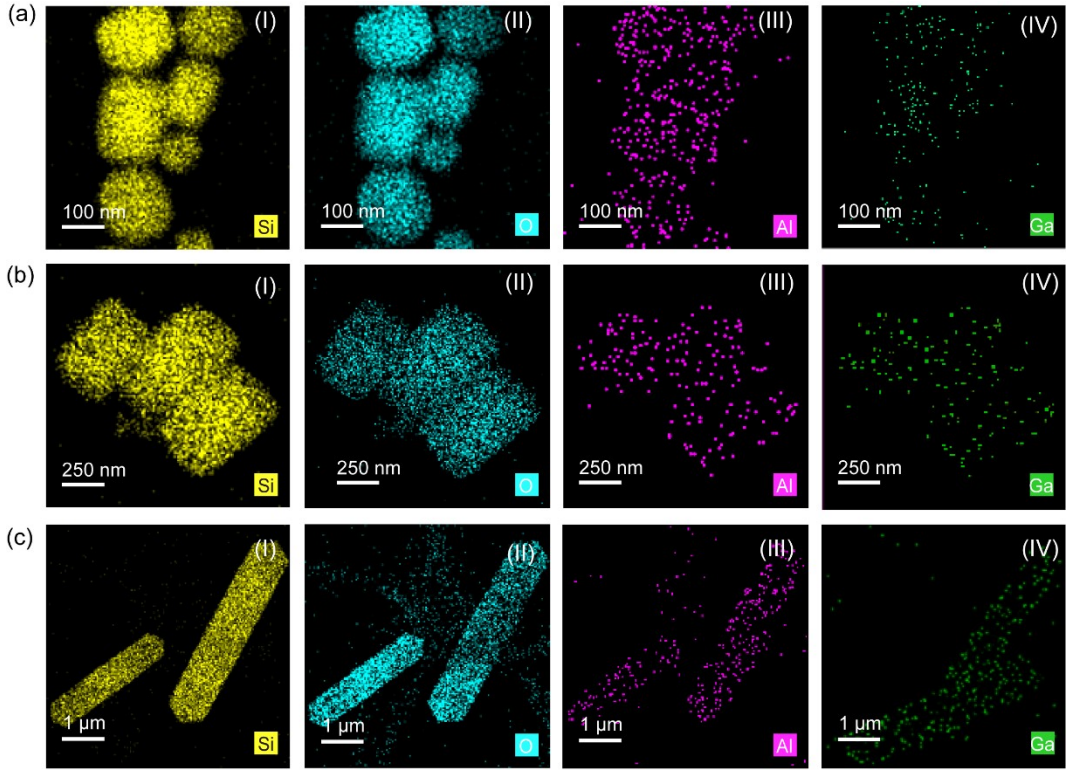

Fig. S2 TEM mapping images of three synthesized Ga/ZSM-5 zeolites: (a) Ga/ZSM-5 (m-ns), (b) Ga/ZSM-5 (h-hexag), and (c) Ga/ZSM-5 (h-coffin) zeolites. (I) Si, (II) O, (III) Al and (IV) Ga element.

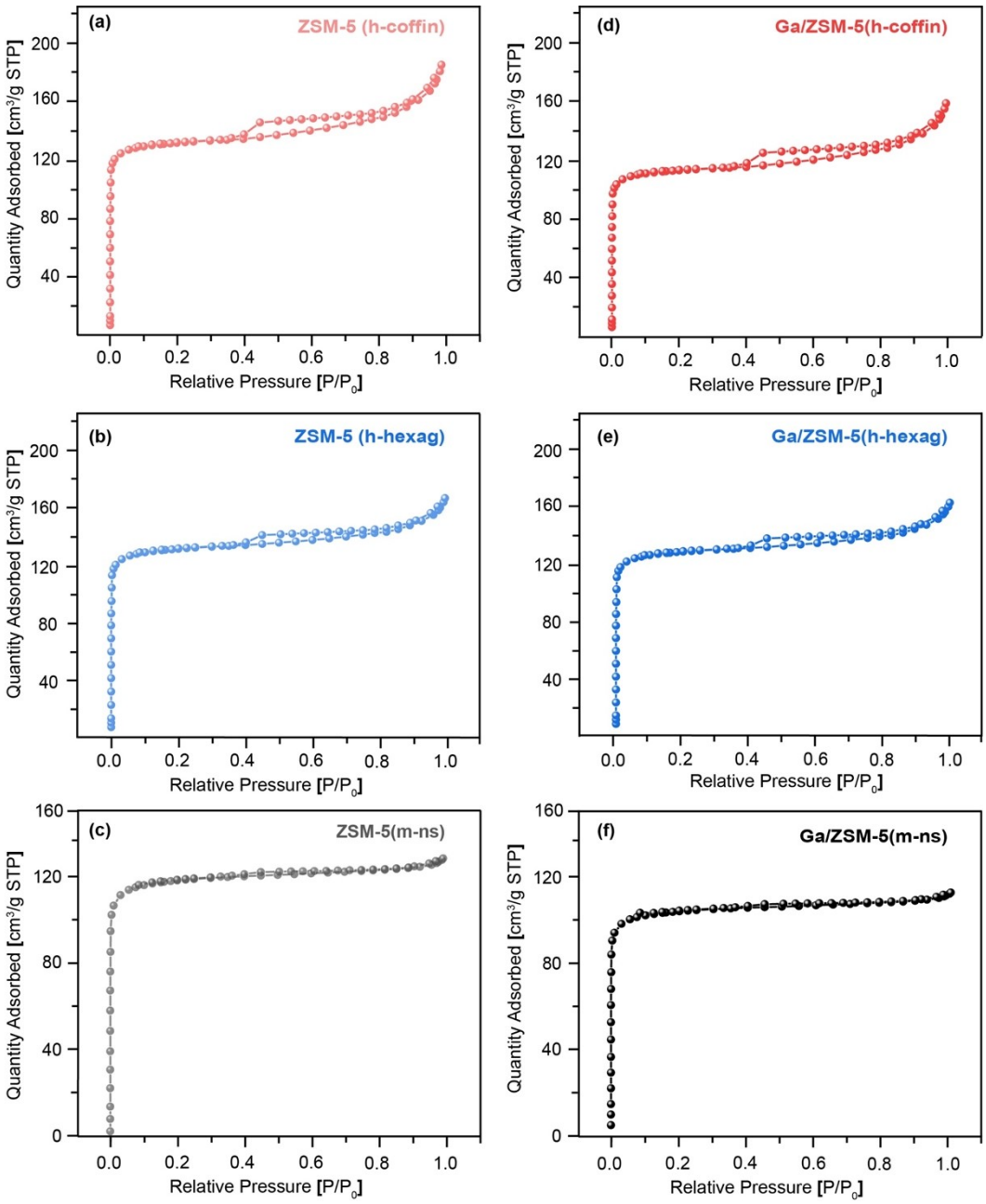

Fig. S3 Ar-adsorption/desorption isotherm of ZSM-5 (m-ns), ZSM-5 (h-hexag), ZSM-5 (h-coffin), Ga/ZSM-5 (m-ns), Ga/ZSM-5 (h-hexag) and Ga/ZSM-5 (h-coffin) zeolites. Also, see **Table 1** for data comparison.

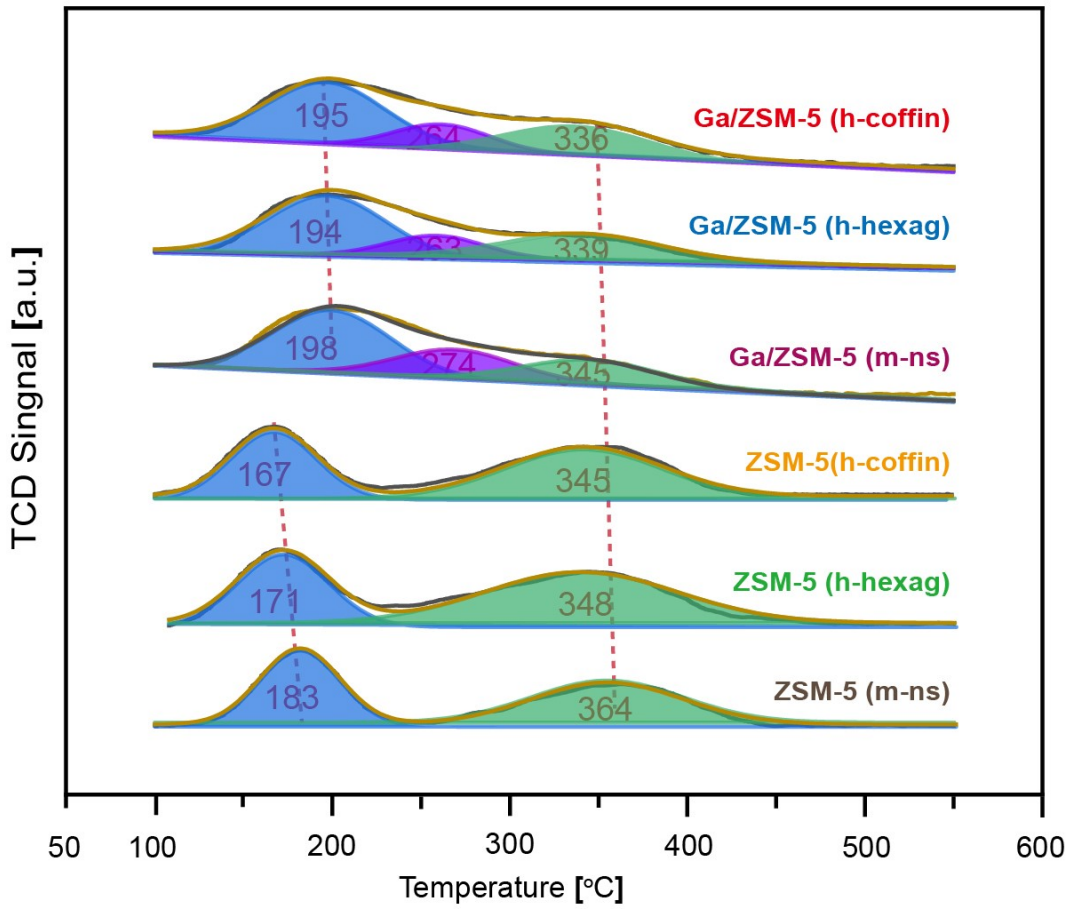

Fig. S4 NH_3-TPD profiles of ZSM-5 (m-ns), ZSM-5 (h-hexag), ZSM-5 (h-coffin), Ga/ZSM-5 (m-ns), Ga/ZSM-5 (h-hexag) and Ga/ZSM-5 (h-coffin) zeolites. Also, see **Table S2** for data comparison.

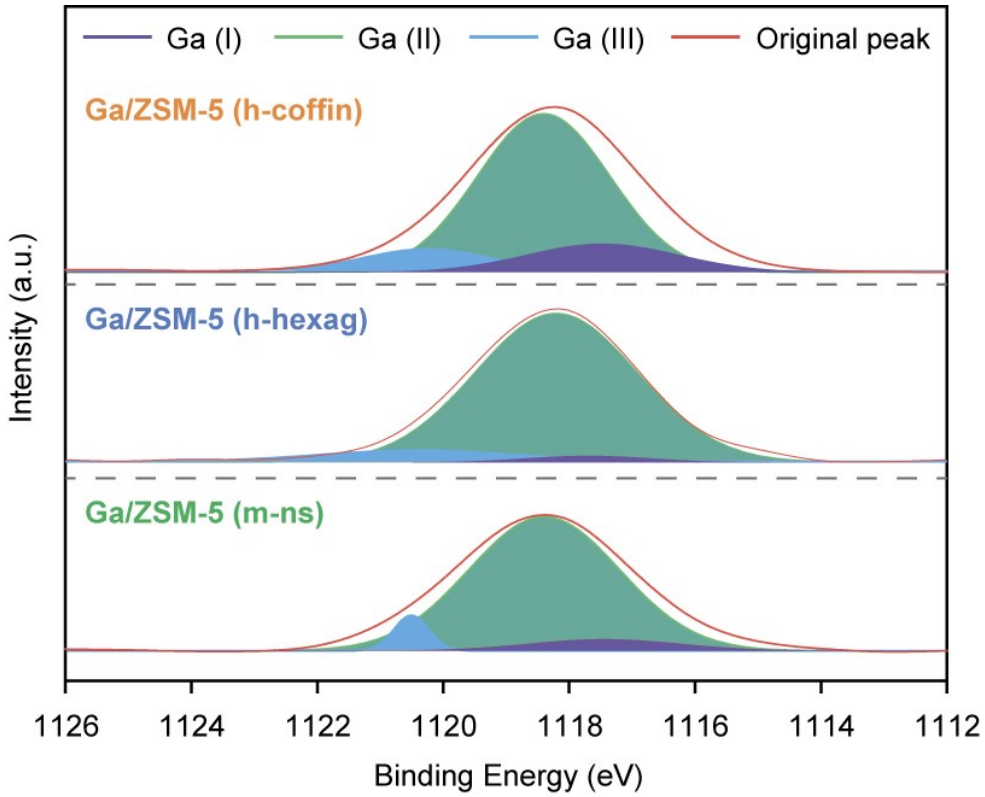

Fig. S5 XPS spectra for $Ga2p_{2/3}$ of Ga/ZSM-5 (m-ns), Ga/ZSM-5 (h-hexag) and Ga/ZSM-5 (h-coffin) zeolites. Ga (I) species: ~ 1117.6 eV; Ga (II) species: ~1118.6 eV; and Ga (III) species: ~1120.4 eV.

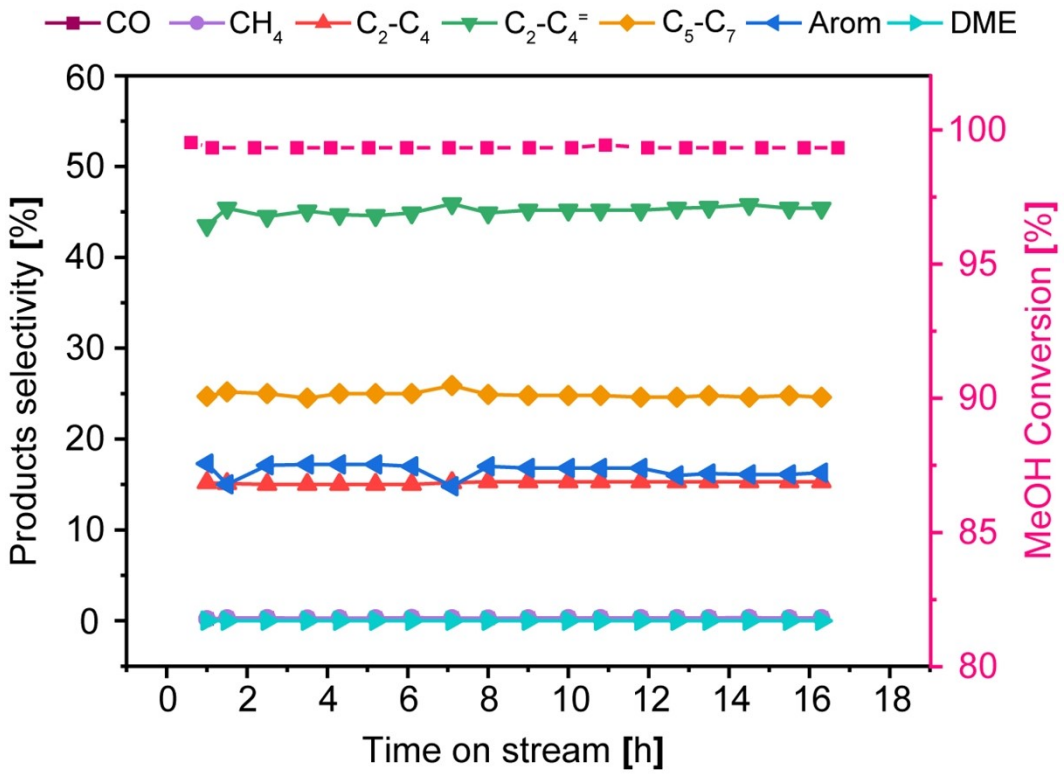

Fig. S6 MTH catalytic test results: products selectivity and methanol conversion of ZSM-5 (m-ns) zeolite over time on stream (WHSV=4 h^{-1}, Reaction temperature=400 °C, Reaction pressure=1 bar).

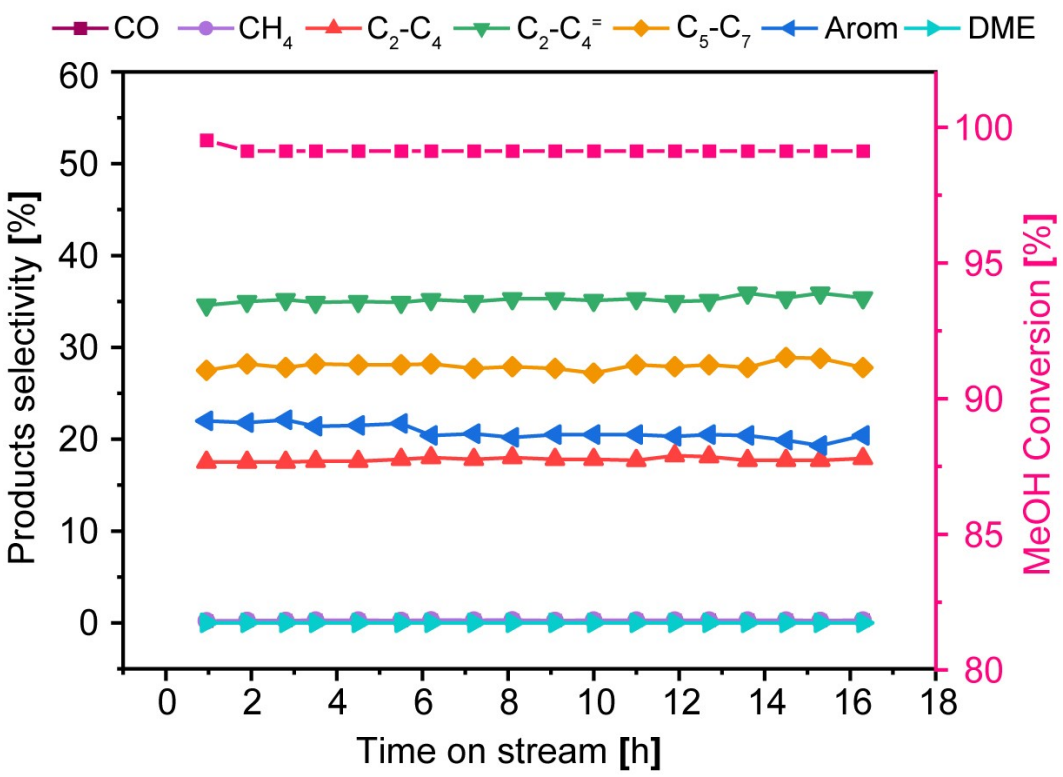

Fig. S7 MTH catalytic test results: products selectivity and methanol conversion of ZSM-5 (h-hexag) zeolite over time on stream (WHSV=4 h^{-1}, Reaction temperature=400 °C, Reaction pressure=1 bar).

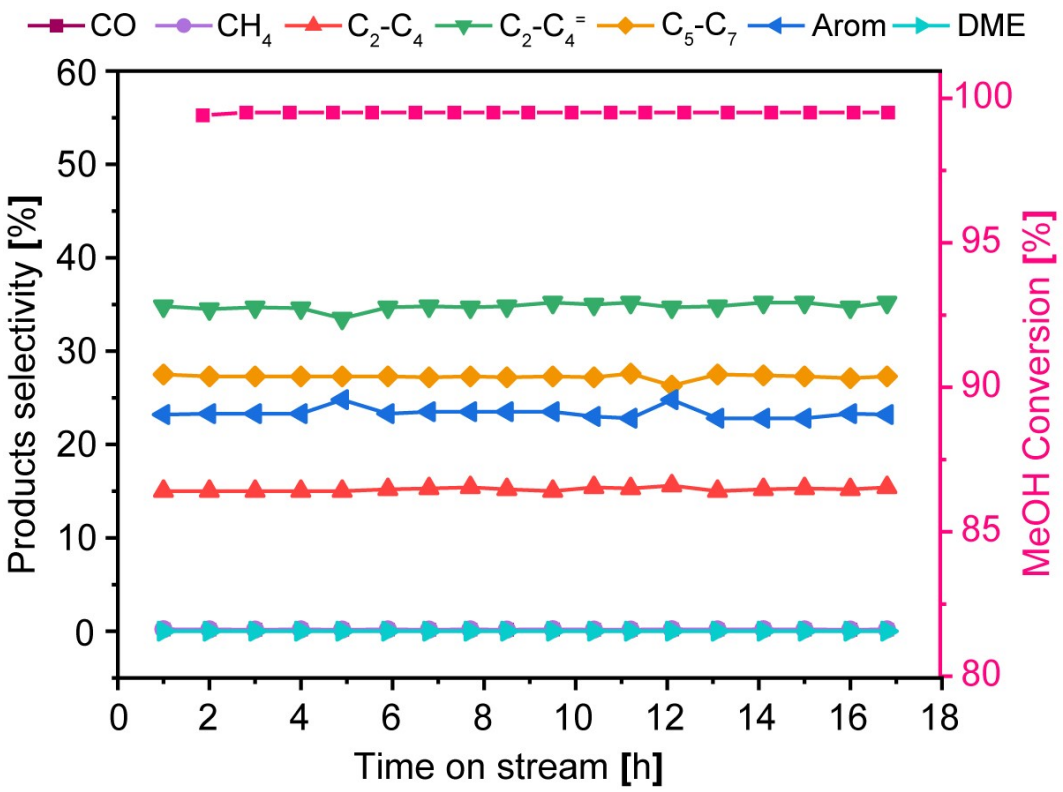

Fig. S8 MTH catalytic test results: products selectivity and methanol conversion of ZSM-5 (h-coffin) zeolite over time on stream (WHSV=4 h^{-1}, Reaction temperature=400 °C, Reaction pressure=1 bar).

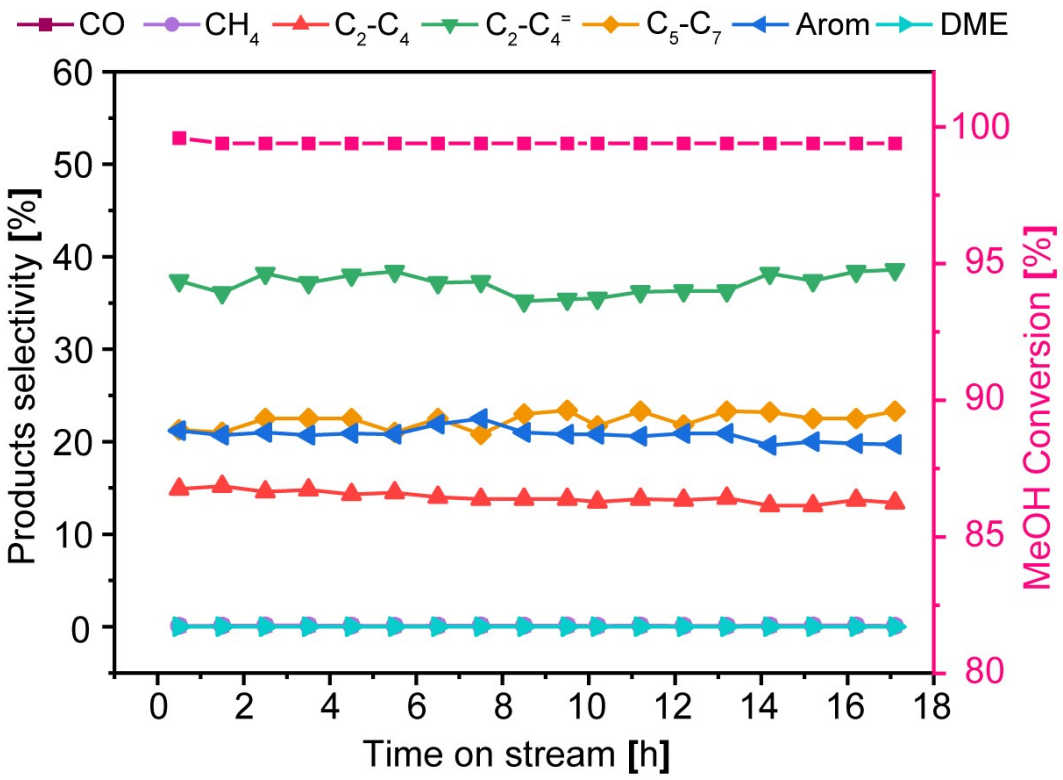

Fig. S9 MTH catalytic test results: products selectivity and methanol conversion of Ga/ZSM-5 (m-ns) zeolite over time on stream (WHSV=4 h^{-1}, Reaction temperature=400 °C, Reaction pressure=1 bar).

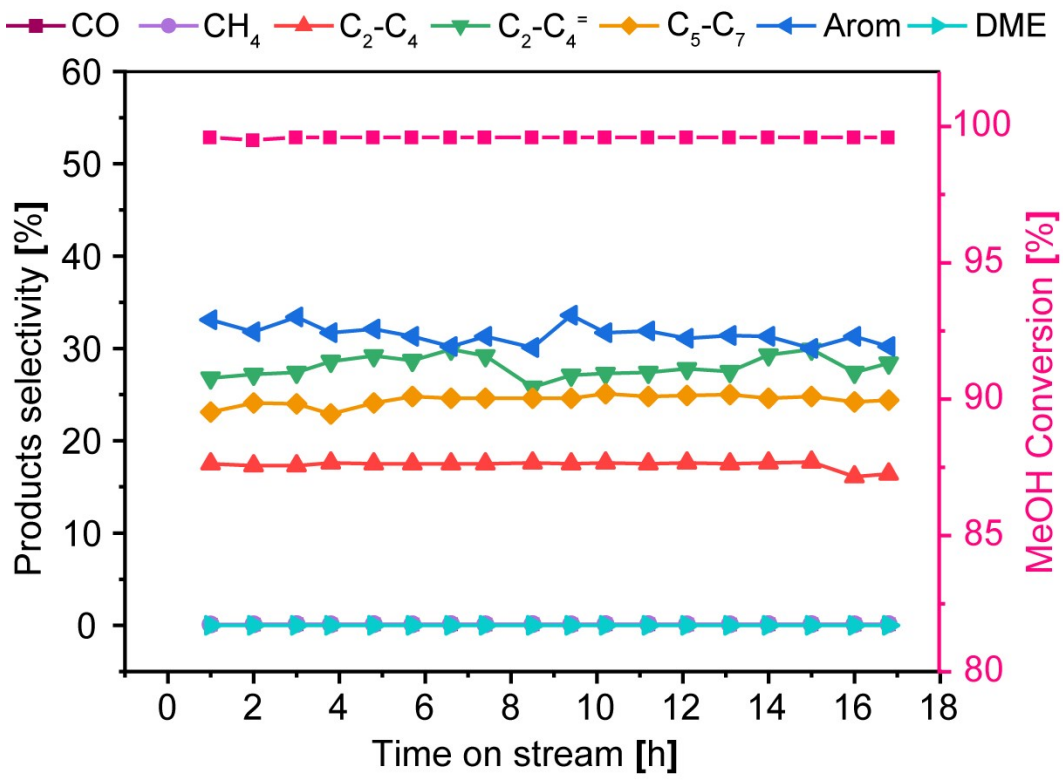

Fig. S10 MTH catalytic test results: products selectivity and methanol conversion of Ga/ZSM-5 (h-hexag) zeolite over time on stream (WHSV=4 h^{-1}, Reaction temperature=400 °C, Reaction pressure=1 bar).

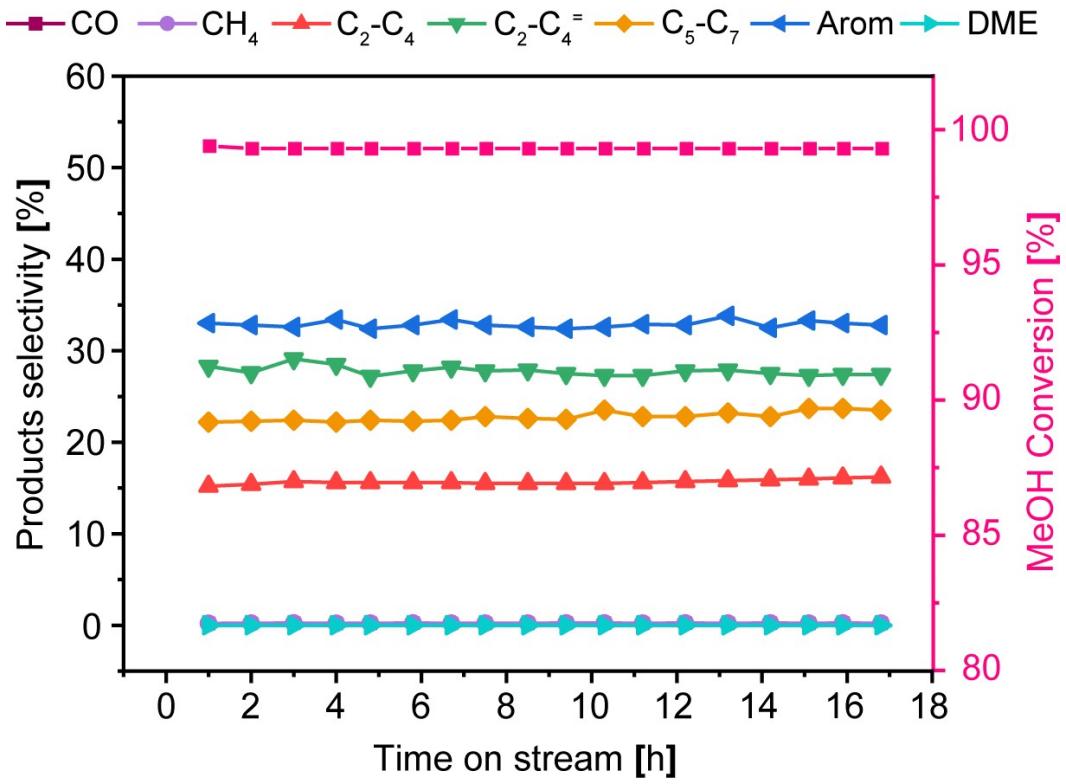

Fig. S11 MTH catalytic test results: products selectivity and methanol conversion of Ga/ZSM-5 (h-coffin) zeolite over time on stream (WHSV=4 h^{-1}, Reaction temperature=400 °C, Reaction pressure=1 bar).

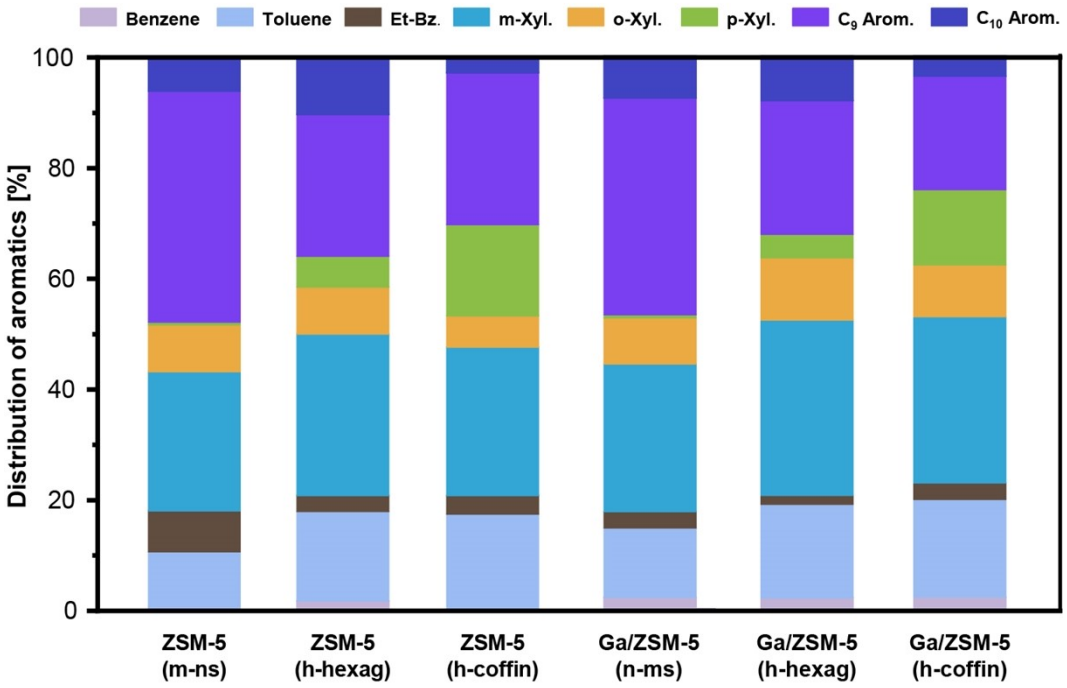

Fig. S12 The MTH product distribution summary within aromatics fractions of ZSM-5 (m-ns), ZSM-5 (h-hexag), ZSM-5 (h-coffin), Ga/ZSM-5 (m-ns), Ga/ZSM-5 (h-hexag) and Ga/ZSM-5 (h-coffin) zeolites at time-on-stream of 12 hours (Reaction conditions: WHSV=4h^{-1}, Reaction temperature=400 °C, Reaction pressure=1bar).

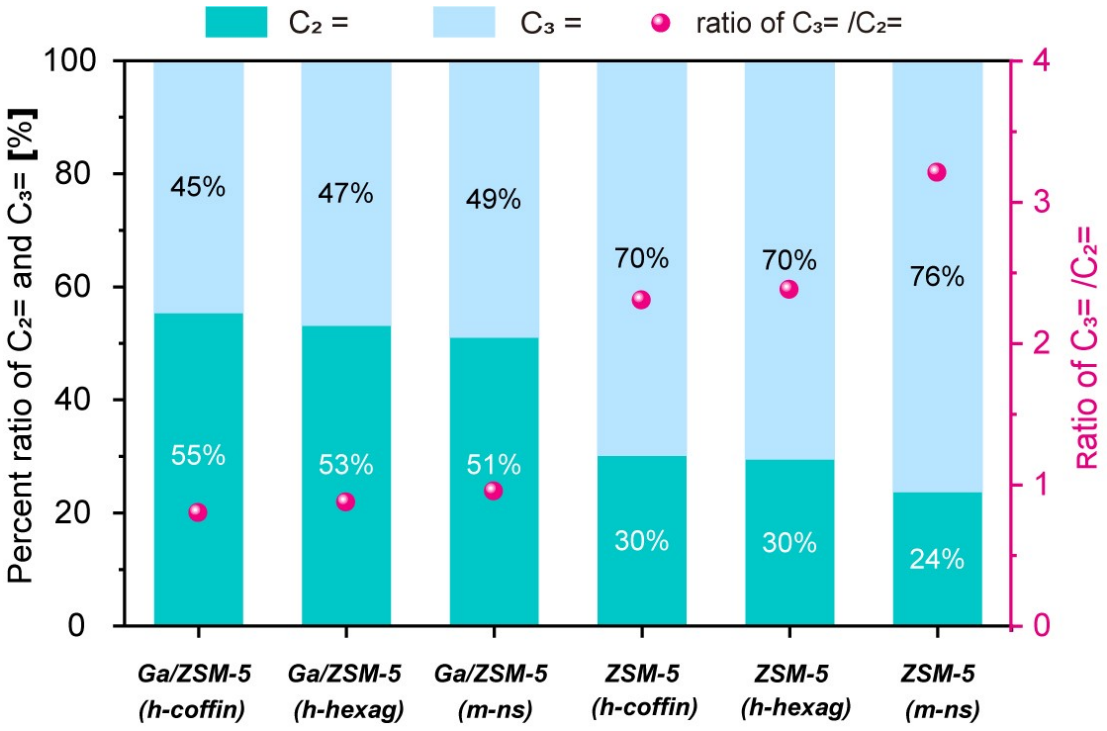

Fig. S13 Propylene-to-ethylene product ratio of ZSM-5 (m-ns), ZSM-5 (h-hexag), ZSM-5 (h-coffin), Ga/ZSM-5 (m-ns), Ga/ZSM-5 (h-hexag) and Ga/ZSM-5 (h-coffin) zeolites at time-on-stream of 12 hours (Reaction conditions: WHSV=4h^{-1}, Reaction temperature=400 °C, Reaction pressure=1 bar).

S3. Supplementary Tables

Table S1. A summary of the literature reported MTA catalytic performance over modified ZSM-5 zeolites.

Ref.	Types of zeolites	Si/ Al (SAR)	Crystal size	Reaction conditions	Aromatics/ BTX selectivity	Lifetime
7	Nano sized hierarchical ZSM-5	25	100 nm	T=450 °C; P=5 bar WHSV=2 h^{-1}	BTX: 37 % Aromatics: 42 %	120 minutes
8	Hollow triple-shelled Zn/MFI zeolites	MFI: ∞ ZSM-5: 24	450 nm	T=475 °C; P=1 bar WHSV=0.8 h^{-1}	Aromatics: 66.9% P-xylene ≥ 35 %	40 hours
9	Core@shell ZSM-5	Shell: 440 Core: 60	600 nm	T=430 °C; P=1 bar WHSV=2 h^{-1}	Aromatics: 28.4%	72.5 hours
10	Hollow ZSM-5	38	40-50 um	T=390 °C; P=5 bar WHSV=3.2 h^{-1}	Aromatics: 40.1%	186 hours
11	Hierarchical ZSM-5 (desilication)	35	400-500 nm	T=400 °C; P=1 bar WHSV=3.16 h^{-1}	BTX: 37.0 % Aromatics: 58.4 %	80 hours
12	Kaolin derived hierarchical ZSM-5	42	-	T=390 °C; P=1 bar WHSV: -	Aromatics: 30+ %	60 hours
13	Hierarchical Zn/ZSM-5	50	250-270 nm	T=450 °C; P=1 bar WHSV=1.9 h^{-1}	Aromatics: 65.8 %	15 hours
14	Hierarchical Zn/MFI NRA	30	240-350 nm	T=475 °C; P=1 bar WHSV=0.75 h^{-1}	Aromatics: 76 %	≥ 40 hours
15	Steam-Treated Zn/ZSM-5	120	150-200 nm	T=430 °C; P=5 bar WHSV=8 h^{-1}	Liquid hydrocarbon: 27 %	120 hours
16	Zn-ZSM-5/Al_2O_3	40	-	T=400 °C; P=20 bar WHSV=5 h^{-1}	Aromatics: 35 %	40 hours
17	Ag/ZSM-5	30	150-200 nm	T=500 °C; P=1 bar WHSV: -	Aromatics: 39.7 %	≥ 12 hours
	Cu/ZSM-5				Aromatics: 53.8 %	
	Ni/ZSM-5				Aromatics: 52.3 %	
	Pd/ZSM-5				Aromatics: 32.1 %	
	Ir/ZSM-5				Aromatics: 28.2 %	
	Ru/ZSM-5				Aromatics: 30.1 %	
18	ZnO/ hierarchical ZSM-5	25	-	T=460 °C; P=0.8 bar WHSV=2 h^{-1}	Aromatics: 69 %	≥ 22 hours
19	P@Zn/ZSM-5	15	-	T=430 °C; P=1 bar WHSV=2 h^{-1}	BTX: 50.6 % Aromatics: 59.7 %	-

20	Zn-Sn/ZSM-5	25	400-600 nm	T=450 °C; P=1 bar WHSV=0.8 h^{-1}	BTX: 64.1 %	16 hours
21	Zn/ZSM-5 Nanosheet	15	50 nm (b-axis)	T=440 °C; P=1 bar WHSV=1 h^{-1}	BTX: 54.5%	100 hours
22	Cd/ZSM-5	19	-	T=420 °C; P=1 bar WHSV=2.1 h^{-1}	Aromatics: 63.0 %	-
23	Ga_2O_3/ZSM-5 Ga/ZSM-5	15	-	T=450 °C; P=1 bar WHSV: -	Aromatics: 43.6 % Aromatics: 51.2 %	≥ 12 hours
24	Ga-Ga/ZSM-5	25	-	T=450 °C; P=1 bar WHSV=5.3 h^{-1}	BTX: 33 %	-
25	Hierarchical Ga/ZSM-5	40	700 nm	T=450 °C; P=1 bar WHSV=4.6 h^{-1}	BTX: 47.4 % Aromatics: 60.1 %	6 - 8 hours
26	H-ZSM-5	50	60 nm 90 nm 400 nm 1.2 um 4.0 um	T=450 °C; P=1 bar WHSV=2.0 h^{-1}	Aromatics: 47 % Aromatics: 43 % Aromatics: 41 % Aromatics: 38 % Aromatics: 32 %	120 mins
27	H-ZSM-5	40	2.0 um 1.0 um 0.5 um 0.25 um	T=390 °C; P=0.5 MPa WHSV=3.2 h^{-1}	Aromatics: 36 % Aromatics: 35 % Aromatics: 34 % Aromatics: 34 %	30 h 40 h 80 h 170 h
28	Ga/ZSM-5 (DeSi)	14	200-400 nm	T=400-500 °C; P=1 bar WHSV=2.37 h^{-1}	Aromatics: 37.2 %	4 hours
29	Hollow-IM-ZSM-5 Sphere-IM-ZSM-5 Rod-IM-ZSM-5 Coffin-IM-ZSM-5	31-32	30–50 μm	T=390 °C; P=0.5 MPa WHSV=3.18 h^{-1}	Aromatics: 38 % Aromatics: 39 % Aromatics: 42 % Aromatics: 48 %	160 h 105 h 65 h 60 h
30	H-ZSM-5	44	0.25 um 2.0 um	-	Aromatics: 34 % Aromatics: 45 %	170 h 40 h
31	Ga/ZSM-5	110	-	T=400 °C;	Aromatics: 47 %	-
Our Work	***Ga/ZSM-5 (n-ns)***	***107***	***110 nm***	***T=400 °C; P=1 bar WHSV=4 h^{-1}***	***BTX distribution: 51 % Aromatics: 21 %***	***> 18 hours***
	Ga/ZSM-5 (h-hexag)	***111***	***450 nm***		***BTX distribution: 66 % Aromatics: 30 %***	
	Ga/ZSM-5 (h-coffin)	***119***	***4600 nm***		***BTX distribution: 73 % Aromatics: 34 %***	

Table S2. Physicochemical properties of as-synthesized ZSM-5 and Ga/ZSM-5 zeolites

Catalysts	Si/Al ratio [a]	Ga (wt%) [b]	Weak acid (μmol·g^{-1}) [c]	Medium acid (μmol·g^{-1}) [c]	Strong acid (μmol·g^{-1}) [c]
ZSM-5 (m-ns)	103	-	143	-	144
ZSM-5 (h-hexag)	108	-	137	-	155
ZSM-5 (h-coffin)	113	-	127	-	159
Ga/ZSM-5 (m-ns)	107	2.03	145	23	24
Ga/ZSM-5 (h-hexag)	111	1.96	134	20	36
Ga/ZSM-5 (h-coffin)	119	2.12	126	19	37

[a] Calculated by XRF. [b] Calculated by ICP. All samples have been dried before testing. The test results have been normalized. [c] Calculated by NH_3-TPD, also refer to Fig. S3.

Table S3. MTH catalytic test results: The results of product distribution at time-on-stream of 12 hours [a].

Samples	C_2-C_4 $^-$ (%)	C_2-C_4 $^=$ (%)	C_5+ paraffins (%)	Aromatics (%)	Species in aromatics (%)		
					BTX (%)	Toluene (%)	Xylenes (%)
ZSM-5 (m-ns)	15	45	23	15	46	12	34
ZSM-5 (h-hexag)	16	36	27	20	59	16	43
ZSM-5 (h-coffin)	15	35	26	22	67	17	50
Ga/ZSM-5 (m-ns)	15	38	25	21	51	12	35
Ga/ZSM-5 (h-hexag)	17	28	24	30	66	16	47
Ga/ZSM-5 (h-coffin)	16	26	23	34	73	18	53

[a] Reaction conditions: WHSV=4 h^{-1}, Reaction temperature=400 °C, Reaction pressure=1 bar.

S4. Supplementary References

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