

Electronic Supplementary Information (ESI) for

**Hierarchical Hollow Al-Rich Nano ZSM-5 Crystals for Highly Selective
Production of Light Olefins from Naphthene**

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1 Experimental Section

Chemicals. Tetraethyl orthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH) and decane were purchased from Beijing InnoChem Science & Technology Co., Ltd. Sodium hydroxide (NaOH), aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) and cobalt nitrate ($\text{Co}(\text{NO}_3)_2$) were purchased from Sinopharm Chemical Reagent Co.,Ltd. Aluminium chloride (AlCl_3) was provided by Guangdong Xilong Chemical Reagent Co.,Ltd. *n*-octane was purchased from Tianjin Damao Chemical Reagent Co.,Ltd. Deionized water (DI) water was used for all experiments.

Preparation of parent ZSM-5 (Z5-LCA). The parent ZSM-5 zeolites containing local concentrated Al (**Z5-LCA**) were prepared as follows. Tetraethyl orthosilicate (TEOS) was added to tetrapropylammonium hydroxide (TPAOH) solution, and the resultant solution was hydrolyzed at 40 °C for 1 h. Then a solution containing aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) and sodium hydroxide (NaOH) were added into the abovementioned mixture and stirred for 1 h at room temperature. The chemical composition of this mother gel was $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{TPAOH}:\text{Na}_2\text{O}:\text{H}_2\text{O} = 25:1:7:3:1800$. The gel was crystallized in a Teflon-lined stainless-steel at 170 °C for 48 h. Afterward, the obtained crystals were filtered and washed with deionization (DI) water until pH reached 8.0. The samples were dried for 12 h at 110 °C and the parent Z5-LCA was prepared by calcination at 550 °C for 4 h in a muffle furnace under air flow. **Four control groups** with the same chemical composition as that of Z5-LCA ($\text{Si}/\text{Al} = 12.5$) were synthesized as follows. **Z5-C1** was obtained using AlCl_3 as the aluminum source instead of $\text{Al}(\text{NO}_3)_3$. **Z5-C2** was synthesized by mixing TEOS and $\text{Al}(\text{NO}_3)_3$ at room temperature for 1 h prior to the addition of TPAOH. **Z5-C3** was prepared by increasing the hydrolysis time of TEOS and TPAOH from 1 h to 8 h at 40 °C. **Z5-C4** was obtained by increasing the incubation time of the mother gel from 1 h to 8 h at room temperature.

Synthesis of hierarchical hollow ZSM-5 by alkaline treatment. Alkaline treatment of the synthesized ZSM-5 crystals (Z5-LCA, Z5-C1, Z5-C2, Z5-C3, Z5-C4 and Z5-32) was performed in 0.2 M or 0.6 M NaOH solution at 80 °C for 30 min. The resultant alkali-treated crystals were washed thoroughly with DI water and dried at 110 °C for 4 h. The obtained crystals were denoted as Z5-LCA-xAT, Z5-C1-xAT, Z5-C2-xAT, Z5-C3-xAT, Z5-C4-xAT and Z5-32-xAT, respectively (x is the concentration of NaOH used in the alkaline treatment process, x = 0.2 or 0.6). Prior to further characterization and catalytic applications, the alkali-treated samples were ion-exchanged with NH₄Cl solution at 70 °C for 40 min, and then were calcined in static air at 550 °C for 2 h (heating rate of 1 °C/min) to obtain proton-type ZSM-5 zeolites. During the alkaline treatment process, multiple samples were collected and immediately centrifugated in order to analysis the concentrations of Si and Al in the filtrates at different times (5 min, 10 min, 15 min, 20 min and 30 min).

Preparation of dehydrated Co(II)-exchanged zeolites. Co(II)-exchanged Z5-LCA zeolites (Co-Z5-LCA) and control zeolites (Co-Z5-C1, Co-Z5-C2, Co-Z5-C3 and Co-Z5-C4) were prepared by ion exchange of synthesized parent ZSM-5 zeolites with 0.05 M Co(NO₃)₂ at room temperature for 8 h. The pH values of the solutions were kept at 5.5 using 0.1 M HNO₃. After ion exchanging, the obtained Co(II)-exchanged ZSM-5 samples were washed three times with DI water and dried at 120 °C. Co-Z5-LCA samples were further dehydrated at 400 °C (under vacuum of 0.02 Pa) for 4 h prior to UV measurements, which were referred to as Co-Z5-LCA-DH.

2 Catalyst characterization

X-ray diffraction (XRD) patterns (2θ ranging from 5° to 35°) were measured by an Empyrean X-ray diffractometer (PANalytical Corporation, Netherland) using Cu K α radiation (tube current 40 mA, voltage 40 kV). The relative crystallinities were calculated by the integral areas of peaks from 22.5° to 25.0° using a standard ZSM-5 as the reference. Crystal size and morphology of the parent and alkali-treated zeolites were investigated

using SEM on a JEOL JSM-6700F electron microscope. The elemental distribution of the synthesized zeolites were determined by scanning transmission electron microscopy (STEM) mapping. X-ray fluorescence (XRF) spectroscopy was used to elemental contents of different samples on a ZSX Primus II (Rigaku) apparatus. BET surface areas were calculated by the Brunauer-Emmett-Teller (BET) method from the N₂ desorption data. The contributions from both micro- and mesoporosity were calculated using the t-plot and the Barrett-Joyner-Halenda (BJH) model. The concentrations of Si, Al and Co in filtrates were analyzed by an inductively coupled plasma spectrometer (5110 ICP, Agilent Technologies). X-ray photoelectron spectroscopy (XPS) spectra were used to analyze the surface elemental contents of the ZSM-5 samples on a Thermo Fisher ESCALAB 250 spectrometer with Al K_α (150W) excitation. The acidic properties of the ZSM-5 zeolites were analyzed by temperature-programed desorption of ammonia (NH₃-TPD) on a Micromeritics Auto chem II 2920 apparatus equipped with a thermal conductivity detector (TCD) unit. The solid-state magic angle spinning (MAS) NMR analyses of the synthesized ZSM-5 samples were performed on a Bruker AVANCE III 600WB spectrometer equipped with a 4 mm triple resonance MAS probe and 7 mm double resonance MAS probe for ²⁷Al and ²⁹Si, respectively. The spinning rates were 5 kHz and 12 kHz corresponding to ²⁹Si and ²⁷Al MAS NMR, respectively. The ²⁷Al MAS NMR spectra were obtained using 0.4 μs ($< \pi/15$) pluses at a resonance frequency field of 156.4 MHz and a recycle delay of 1 s. The ²⁹Si MAS NMR spectra were obtained using 1.8 μs pluses at a resonance frequency field of 99.3 MHz. Diffuse reflection UV (DR-UV) spectra of Co-Z5-DH samples were measured by a Cary Series UV-VIS Spectrometer (Agilent Technologies) equipped with a DR attachment with BaSO₄ coated integrating sphere. The spectra were measured in the F-R mode using dehydrated parent ZSM-5 samples as references. The distribution of Al species were calculated according to the method reported by Wichterlová et. al.¹

3 Catalytic tests

The cracking reactions of *n*-octane (C₈H₁₈), decalin (C₁₀H₈) and naphtha feedstocks catalyzed by different ZSM-5 samples were performed in a fixed-bed continuous-flow reactor (with a quartz tube of 10 mm). In a typical run, 0.3 g of ZSM-5 catalyst was put in the flat-temperature zone of the reactor tube, and the oil feedstock (with a catalyst to oil mass ratio, i.e., C/O at 0.30) was injected by a KD Scientific Syringe pump to provide a reaction WHSV up to 480 h⁻¹. The catalytic reactions were conducted at 550 °C or 600 °C under atmospheric pressure, and a refinery gas chromatography with four valves and five columns was used to analyze the gas products. The liquid products were detected by a GC equipped with a capillary column for PONA analysis.

4 Calculation of the distribution of Al species

The distribution of Al species in ZSM-5 framework were calculated according to the method reported by Wichterlová et. al.¹ See supporting information for details. Briefly, the comprehensive FR signal in the region of 13500~23000 cm⁻¹ was resolved to seven Gaussian bands, representing Co(II) ions at three typical cationic sites (α , β , γ) in ZSM-5 framework (**Table S1**). The concentrations of Al_{pair}, Al_{unpair} and Al_{single} were calculated as follows.

$$[\text{Al}_{\text{total}}] = [\text{Al}_{\text{pair}}] + [\text{Al}_{\text{unpair}}] + [\text{Al}_{\text{single}}]$$

$$[\text{Al}_{\text{pair}}] + [\text{Al}_{\text{unpair}}] = 2 \times [\text{Co}]_{\text{loaded}}$$

$$[\text{Al}_{\text{pair}}] = 2 \times ([\text{Co}_{\alpha}] + [\text{Co}_{\beta}] + [\text{Co}_{\gamma}])$$

where [Co]_{loaded} represented the Co(II) exchange capacity in ZSM-5 samples, which can be obtained by calculating the decreased Co(II) amount in Co(NO₃)₂ exchange solutions; [Al_{total}] represented the total Al atom quantity in ZSM-5 samples, which could be calculated based on the molar ratio of Co/Al measured by X-ray fluorescence (XRF); [Co_α], [Co_β] and [Co_γ] represented Co(II) ions coordinated at α , β and γ , respectively, which can be calculated as follows.

$$[Co_{\alpha}] = \varepsilon_1 A_1$$

$$[Co_{\beta}] = \varepsilon_2 A_2 + \varepsilon_3 A_3 + \varepsilon_4 A_4 + \varepsilon_5 A_5$$

$$[Co_{\gamma}] = \varepsilon_6 A_6 + \varepsilon_7 A_7$$

Supplementary Tables

Table S1. Peak positions and corresponding extinction coefficients (ϵ) of Co(II) ions coordinated at α , β and γ sites.

No.	Type	Peak center (cm ⁻¹) ^[a]	ϵ (mmol·cm/g)
Peak 1	Co $_{\alpha}$	~15100	3.5×10^{-3}
Peak 2	Co $_{\beta}$	~16000	1×10^{-3}
Peak 3	Co $_{\beta}$	~17150	1×10^{-3}
Peak 4	Co $_{\beta}$	~18600	1×10^{-3}
Peak 5	Co $_{\beta}$	~21200	1×10^{-3}
Peak 6	Co $_{\gamma}$	~20100	9×10^{-4}
Peak 7	Co $_{\gamma}$	~22000	9×10^{-4}

^[a] The central positions of the resolved Gaussian bands may vary a little in different cases.

Table S2. Co(II) ion exchange capacities and Al species in the framework of different parent ZSM-5 samples

Sample	Co/Al ^[a]	Co _{loaded} (mmol/g)	Al _{total} (mmol/g)	Al _{pair} (%)	Al _{unpair} (%)	Al _{single} (%)
Z5-LCA	0.247	0.896	3.6	49	0	51
Z5-C1	0.125	0.561	4.5	17	8	75
Z5-C2	0.086	0.876	10.2	16	1	83
Z5-C3	0.118	0.277	2.4	23	1	76
Z5-C4	0.117	0.305	2.6	16	7	77

^[a] Molar ratio of Co/Al measured by X-ray fluorescence (XRF).

Table S3. Calculated Al_{pair} species in different ZSM-5 samples

Sample	[Al] _α (mmol/g)	[Al] _β (mmol/g)	[Al] _γ (mmol/g)
Z5-LCA	0.53	1.18	0.08
Z5-C1	0.22	0.40	0.15
Z5-C2	0.31	0.97	0.33
Z5-C3	0.20	0.28	0.04
Z5-C3	0.00	0.37	0.05

Note: [Al]_α = 2 × [Co]_α, [Al]_β = 2 × [Co]_β, [Al]_γ = 2 × [Co]_γ

Table S4. Chemical compositions (Si/Al molar ratio) of different ZSM-5 samples

Sample	by XRF	by EDX	by XPS
Z5-LCA	12.47	11.35	10.01
Z5-C1	12.73	12.03	10.88
Z5-C2	12.52	11.98	11.56
Z5-C3	12.27	11.57	11.48
Z5-C4	12.37	11.73	10.95

Table S5. Textual and chemical properties of ZSM-5 zeolites and alkali-treated samples

Sample	$S_{\text{BET}}^{[a]}$ (m ² /g)	$S_{\text{micro}}^{[b]}$ (m ² /g)	$S_{\text{meso}}^{[c]}$ (m ² /g)	$V_{\text{total}}^{[d]}$ (cm ³ /g)	$V_{\text{micro}}^{[b]}$ (cm ³ /g)	$V_{\text{meso}}^{[e]}$ (cm ³ /g)
Z5-LCA	328	288	40	0.20	0.13	0.06
Z5-LCA-0.2AT	331	267	64	0.22	0.12	0.10
Z5-LCA-0.6AT	384	237	147	0.42	0.12	0.30
Z5-C1	338	302	37	0.21	0.14	0.07
Z5-C1-0.6AT	395	278	117	0.41	0.13	0.29
Z5-C2	320	294	25	0.18	0.14	0.04
Z5-C2-0.6AT	380	275	105	0.36	0.13	0.23
Z5-C3	321	291	30	0.17	0.13	0.04
Z5-C3-0.6AT	368	258	110	0.32	0.12	0.20
Z5-C4	332	299	33	0.21	0.14	0.07
Z5-C4-0.6AT	405	286	119	0.41	0.13	0.28

^[a] Brunauer-Emmett-Teller (BET) method. ^[b] *t*-plot method. ^[c] $S_{\text{BET}}-S_{\text{micro}}$. ^[d] Volume of N₂ adsorbed at $P/P_0 = 0.99$. ^[e] $V_{\text{total}}-V_{\text{micro}}$

Table S6. Acid properties obtained from pyridine adsorption experiments

Sample	Total acidity ^[a] ($\mu\text{mol/g}$)	Total acidity ^[a] ($\mu\text{mol/g}$)		Strong acid site ^[b] ($\mu\text{mol/g}$)	
		Brönsted	Lewis	Brönsted	Lewis
Z5-LCA	220.5	174.6	45.9	155.8	40.6
Z5-LCA-0.6AT	362.8	200.8	162	153.1	124.5
Z5-C1	450.2	391.1	59.1	344.9	48.4
Z5-C1-0.6AT	266.2	151.9	114.3	118.8	91.9
Z5-C2	373.6	293.6	80.0	253.3	65.6
Z5-C2-0.6AT	282	164.3	117.7	127.1	96.6
Z5-C3	254.4	194.1	60.3	167.6	48.9
Z5-C3-0.6AT	329.6	208.7	120.9	168.8	98.9
Z5-C4	338.5	264.0	74.5	221.8	58.9
Z5-C4-0.6AT	277.5	163.5	114.0	128.3	94.0

^{[a],[b]} Brönsted and Lewis acidity determined by pyridine adsorption (200 °C) using FT-IR spectroscopy. ^[b] Strong Brönsted and Lewis acidity determined by pyridine adsorption (350 °C) using FT-IR spectroscopy.

Table S7. Selectivities of ethylene and propylene in the cracking reactions of n-octane and decalin catalyzed by Z5-LCA and Z5-LCA-0.6AT

Catalyst	Feedstock	T (°C)	Conversion Rate (%)	Selectivity (%) ^[a]	
				C ₂ H ₄	C ₃ H ₆
Z5-LCA	n-octane	550	55.07	0.06	0.17
		600	63.53	0.09	0.20
	decalin	550	3.65	0.06	0.12
		600	8.73	0.09	0.12
Z5-LCA-0.6AT	n-octane	550	48.50	0.07	0.19
		600	56.57	0.10	0.23
	decalin	550	6.66	0.08	0.09
		600	12.95	0.17	0.22

Note: ^[a] selectivity = yield/(conversion rate)

Table S8. Diffusion coefficients of two ZSM-5 samples

Zeolite	Diffusion coefficient ^[a]	
	n-octane	ethylcyclohexane
Z5-LCA	0.0346	0.0156
Z5-LCA-0.6AT	0.0460	0.0319

Note: ^[a] Diffusion coefficients are measured by the zero length column (ZLC) method.²⁻³

Table S9. Contents of different Si species in ZSM-5 samples

ZSM-5 sample	Si species (%) ^[a]		
	Si(2Al)	Si(1Al)	Si(0Al)
Z5-LCA	1.27	14.1	84.60
Z5-C1	0.73	8.61	90.66
Z5-C2	0.64	7.61	91.74
Z5-C3	0.36	10.36	89.29
Z5-C4	0.55	7.28	92.17

Note: ^[a] The contents of different Si species are calculated using NMR analysis software Nuts.

Supplementary Figures

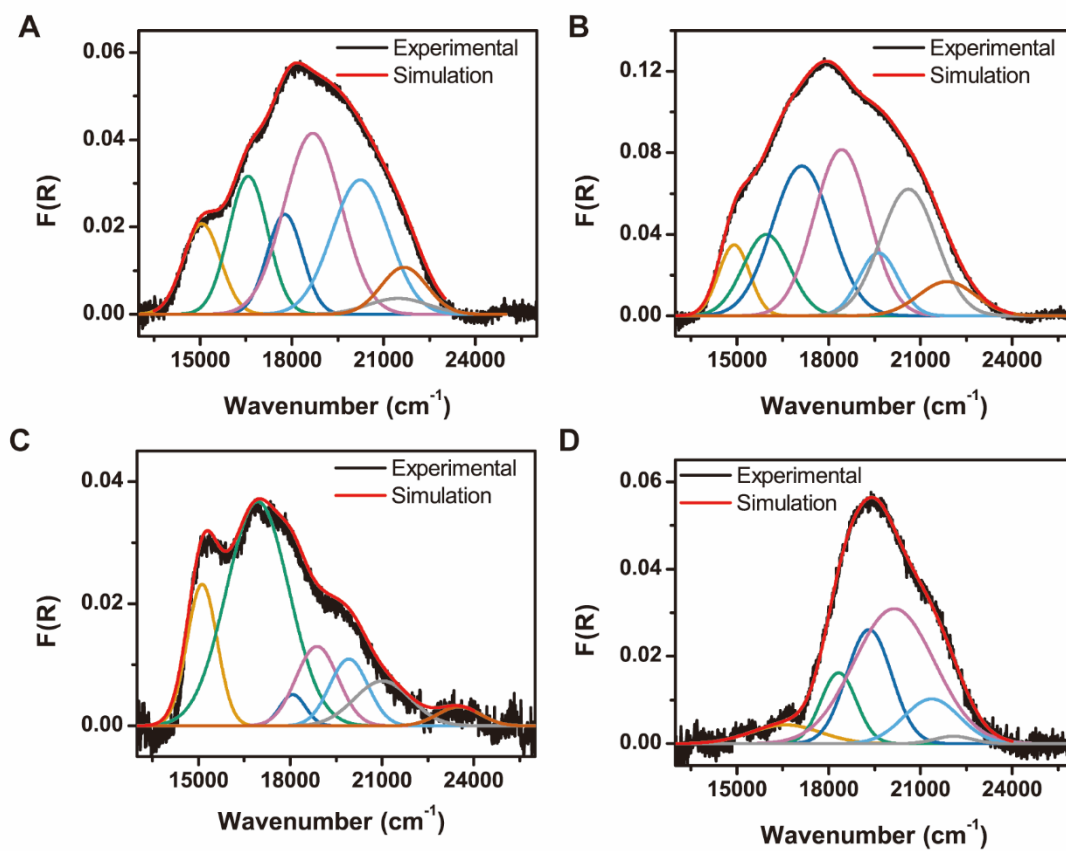


Fig. S1 Decomposition of the DR-UV spectra of four control groups. **(A)** Co-Z5-C1, **(B)** Co-Z5-C2, **(C)** Co-Z5-C3 and **(D)** Co-Z5-C4.

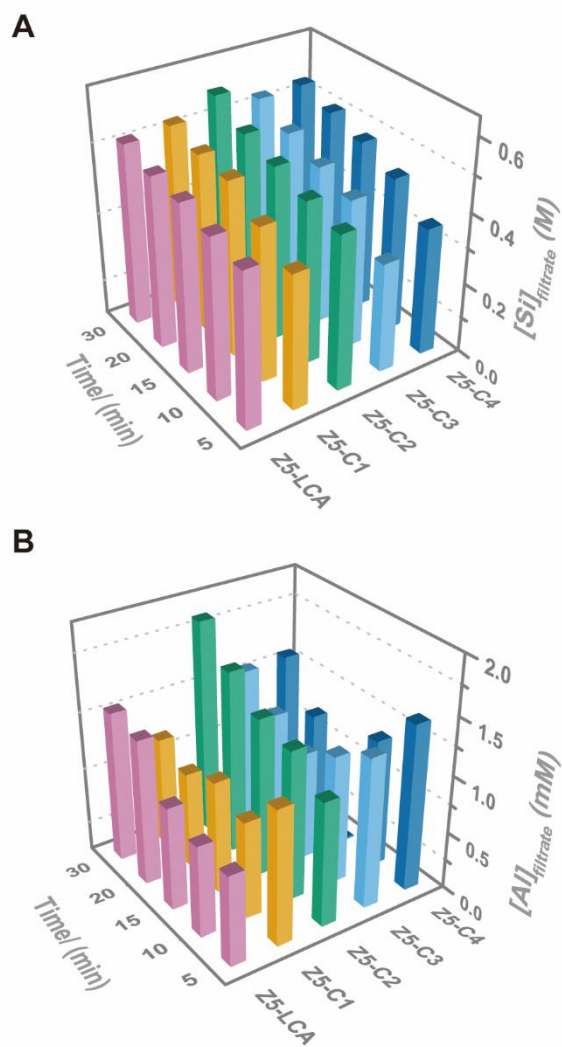


Fig. S2 Variations of (A) Si and (B) Al concentrations in the filtrates of Z5-LCA and four control groups (Z5-C1, Z5-C2, Z5-C3 and Z5-C4) against alkali-treatment time.

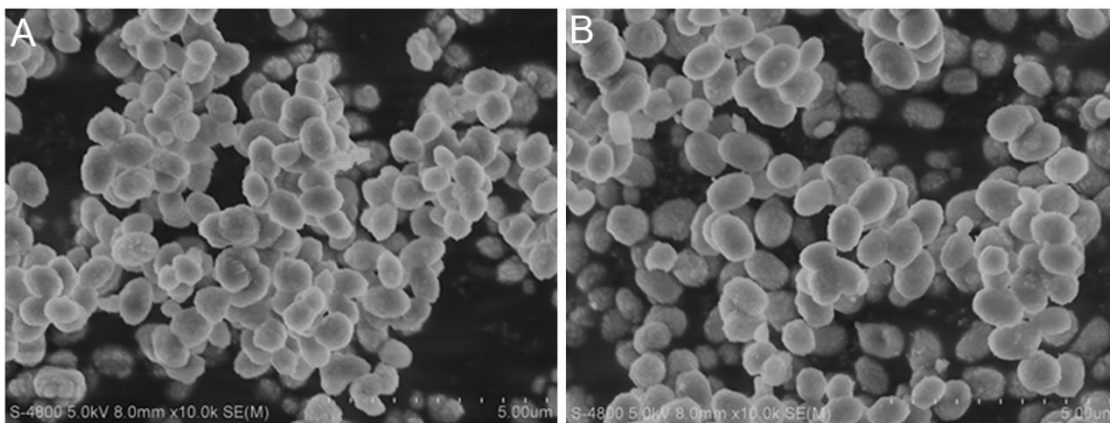


Fig. S3 SEM images of **(A)** Z5-LCA and **(B)** Z5-LCA-0.6AT.

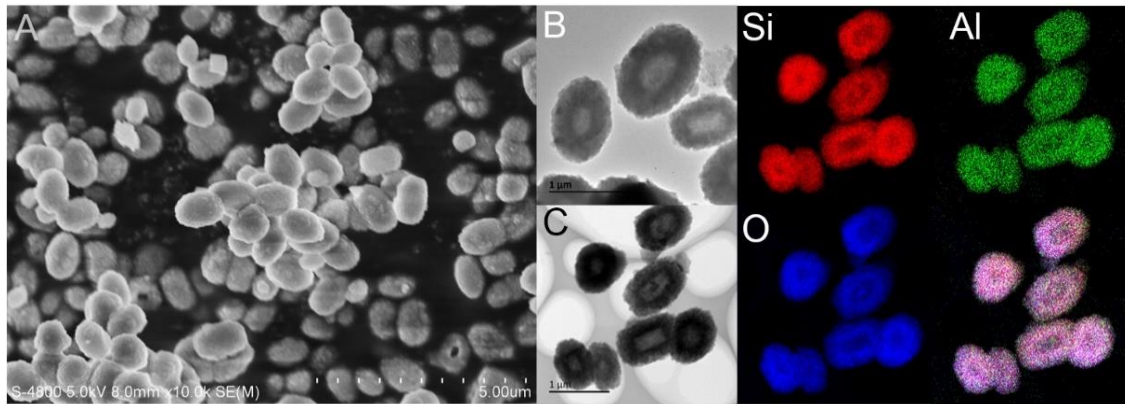


Fig. S4 (A) SEM, (B) HRTEM and (C) element mapping images of Z5-LCA-0.2AT.

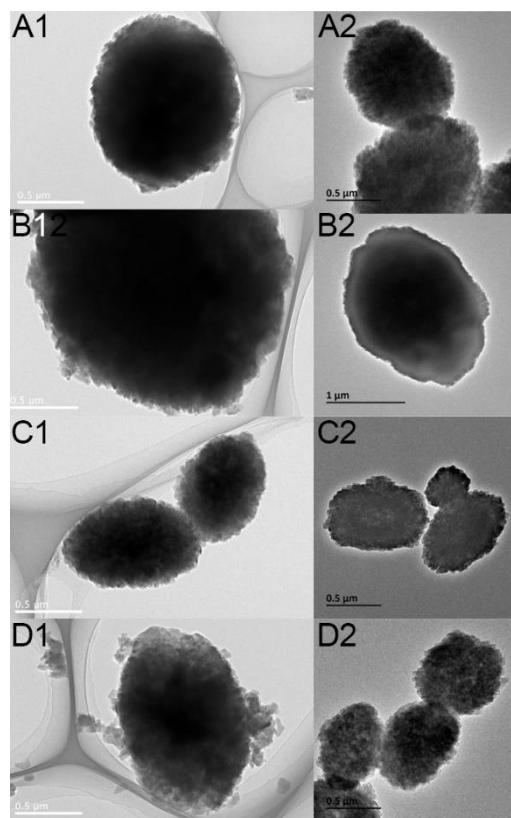


Fig. S5 HRTEM images of ZSM-5 samples in four control groups: **(A1)** Z5-C1, **(A2)** Z5-C1-0.6AT, **(B1)** Z5-C2, **(B2)** Z5-C2-0.6AT, **(C1)** Z5-C3, **(C2)** Z5-C3-0.6AT, **(D1)** Z5-C4 and **(D2)** Z5-C4-0.6AT.

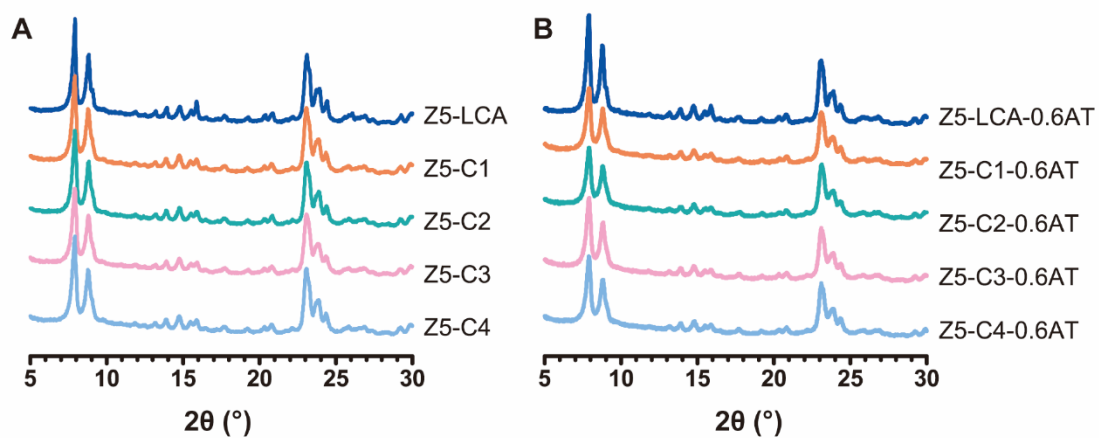


Fig. S6 XRD patterns of (A) synthesized parent ZSM-5 samples (Z5-LCA, Z5-C1, Z5-C2, Z5-C3, Z5-C4) and (B) alkaline-treated ZSM-5 samples (Z5-LCA-0.6AT, Z5-C1-0.6AT, Z5-C2-0.6AT, Z5-C3-0.6AT, Z5-C4-0.6AT).

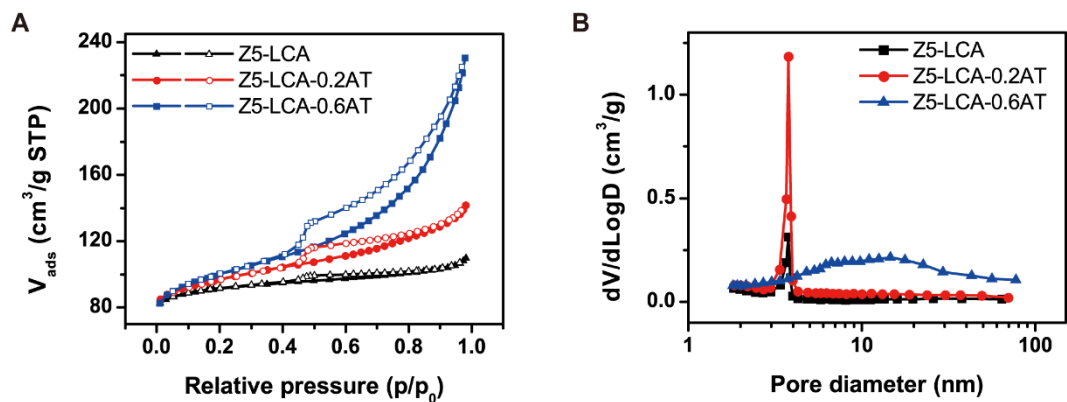


Fig. S7 (A) N₂ adsorption-desorption isotherms. (B) Barrett–Joyner–Halenda (BJH) pore distribution profiles of Z5-LCA, Z5-LCA-0.2AT and Z5-LCA-0.6AT.

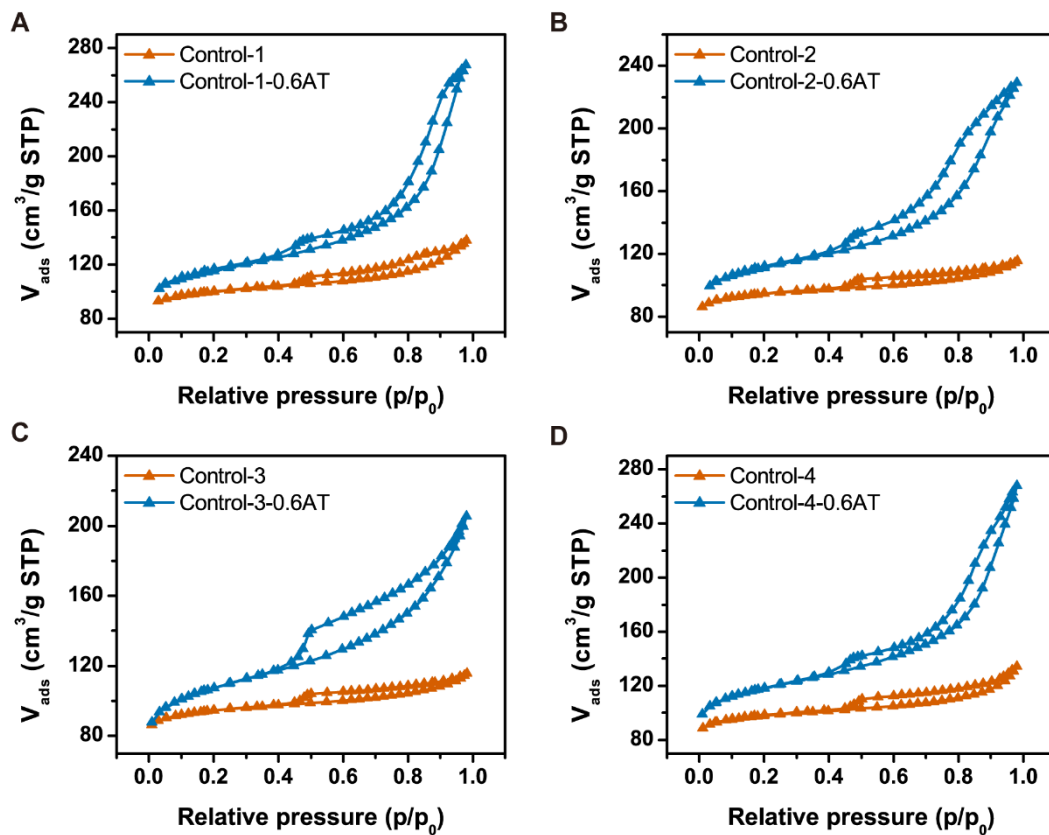


Fig. S8 N_2 adsorption-desorption isotherms of ZSM-5 samples in four control groups. (A) Z5-C1 and Z5-C1-0.6AT, (B) Z5-C2 and Z5-C2-0.6AT, (C) Z5-C3 and Z5-C3-0.6AT and (D) Z5-C4 and Z5-C4-0.6AT.

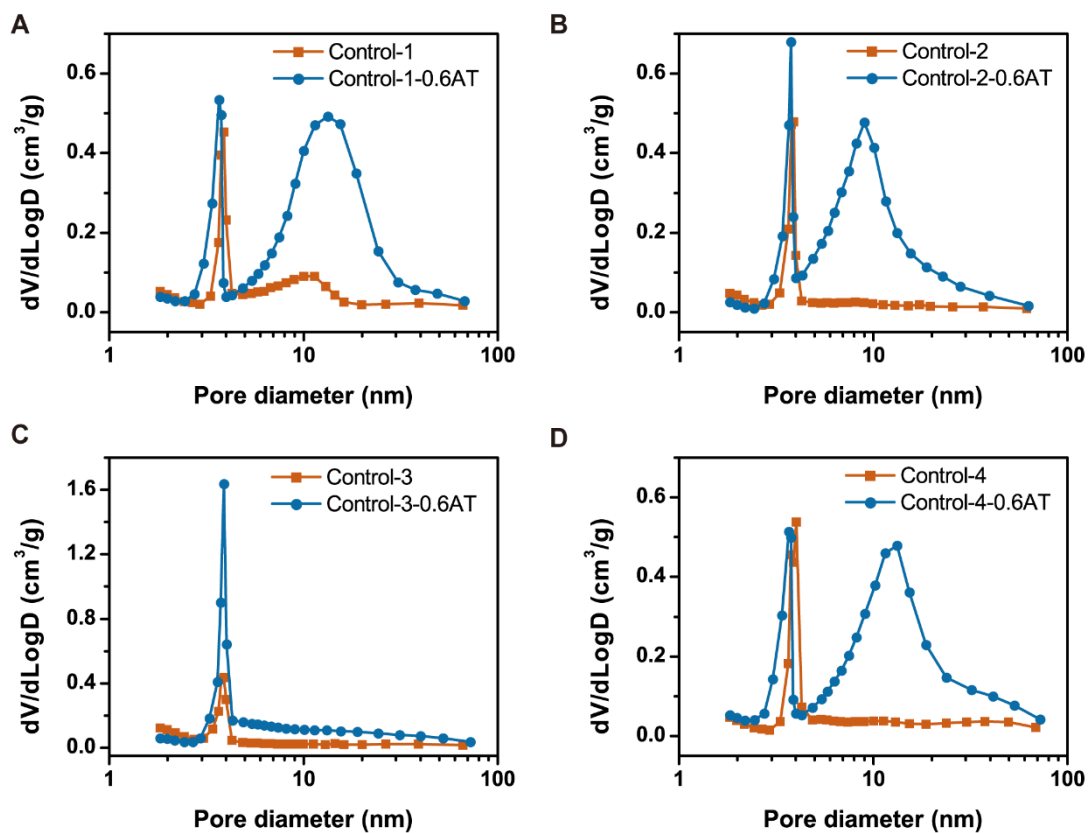


Fig. S9 Barrett–Joyner–Halenda (BJH) pore distributions profiles of ZSM-5 samples in control samples. **(A)** Z5-C1 and Z5-C1-0.6AT, **(B)** Z5-C2 and Z5-C2-0.6AT, **(C)** Z5-C3 and Z5-C3-0.6AT and **(D)** Z5-C4 and Z5-C4-0.6AT.

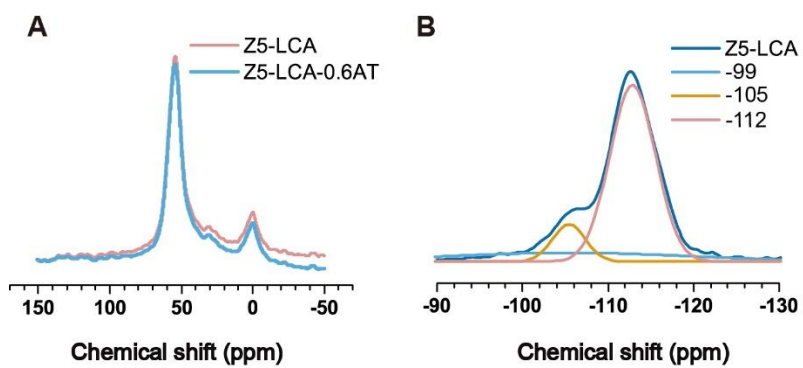


Fig. S10 (A) ^{27}Al MAS NMR spectra of Z5-LCA and Z5-LCA-0.6AT. (B) ^{29}Si MAS NMR spectra of Z5-LCA.

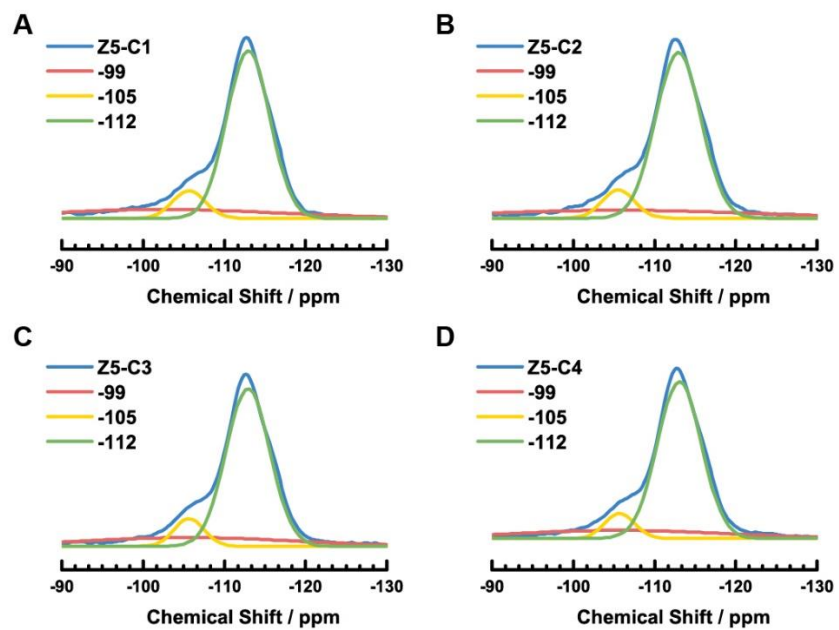


Fig. S11 ^{29}Si MAS NMR spectra of (A) Z5-C1, (B) Z5-C2, (C) Z5-C3 and (D) Z5-C4.

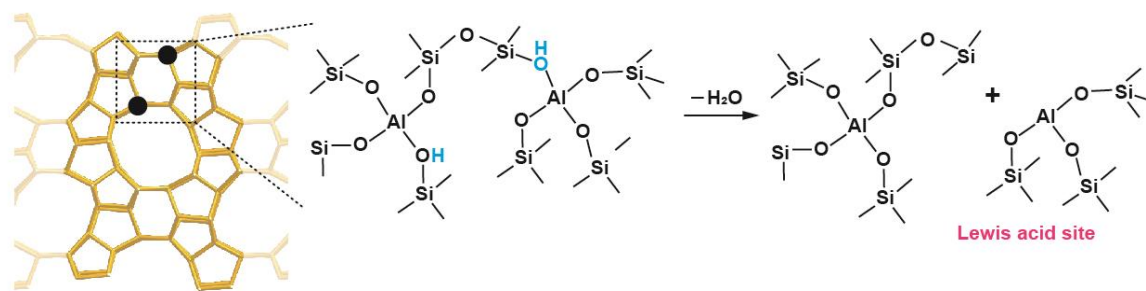


Fig. S12 Schematic illustration of the strong Lewis acid site formed in Z5-LCA.

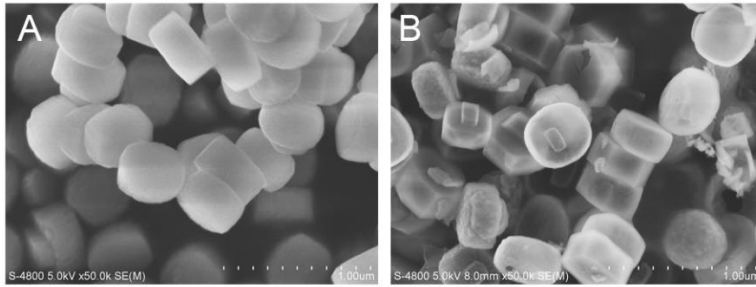


Fig. S13 SEM images of (A) Z5-32 and (B) Z5-32-0.6AT

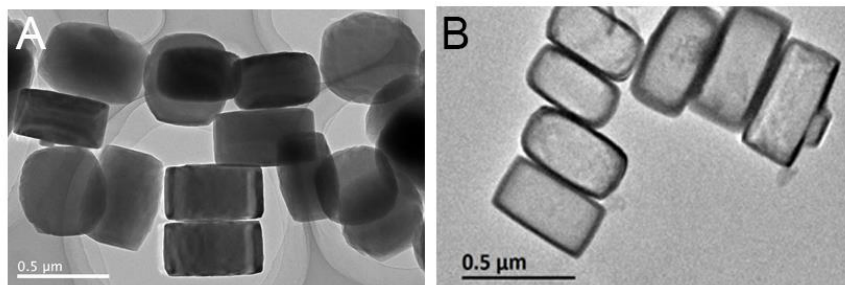


Fig. S14 TEM images of (A) Z5-32 and (B) Z5-32-0.6AT

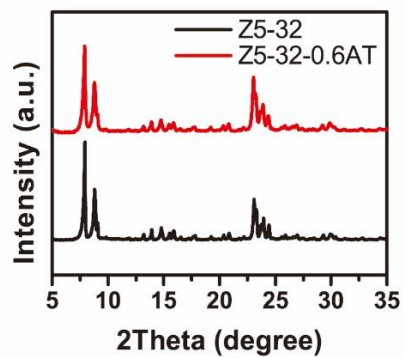


Fig. S15 XRD patterns of (A) Z5-32 and (B) Z5-32-0.6AT

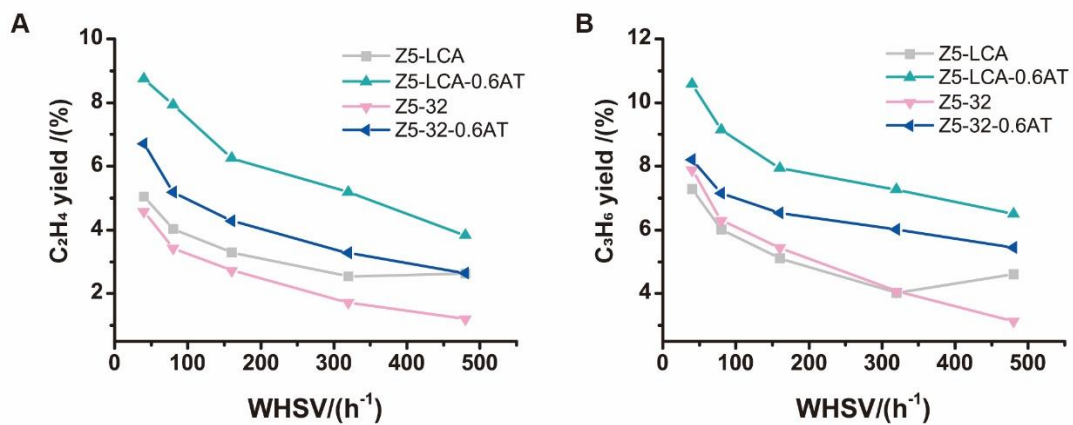


Fig. S16 (A) Ethylene and (B) propylene yields in the cracking reactions of naphtha feedstocks catalyzed by different ZSM-5 zeolites.

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