Supporting information for

SEED-SOL-ASSISTED CONSTRUCTION OF COFFIN-SHAPED MULTILAMELLAR ZSM-5 SINGLE CRYSTAL WITH CTAB

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S1. Experimental

S1.1 Materials

Tetrapropylammonium hydroxide, 25% w/w aqueous solution (TPAOH, analytical grade) was purchased from Aladdin Chemical Reagent Ltd. Aluminum isopropoxide ($C_9H_{21}AIO_3$, analytical grade), tetraethyl orthosilicate (TEOS, analytical grade), ammonia chloride (NH₄Cl, analytical grade), potassium hydroxide (KOH, analytical grade), hexadecyl trimethyl ammonium bromide (CTAB, analytical grade) and methanol (CH₃OH, analytical grade) were purchased from Sinopharm Chemical Reagent Ltd., China. Deionized (DI) water was used for all experiments. Commercial ZSM-5 zeolite (CZSM-5, SiO₂/Al₂O₃ = 36) was purchased from Catalyst plant of Nankai University. S1.2 Preparation of silicalite-1 seed sol

Silicalite-1 seed-sol was synthesized with a molar ratio of 9 TPAOH: 25 SiO₂: 100 EtOH: 480 H₂O. In brief, 19.94 g of TEOS was added dropwise to the mixture of 27.97 g of TPAOH and 12.10 g of DI water at room temperature with vigorous stirring. After complete hydrolysis of TEOS at room temperature for 24 h, the obtained mixture was transferred into a 50 mL Teflon lined stainless-steel autoclave and hydrothermally treated at 353 K for 24 h. The resultant silicalite-1 seed sol was directly used for the synthesis of CMZS without any additional purification. S1.3 Synthesis of CMZS zeolite

Firstly, 0.92 g of KOH pellet was dissolved in 35.62 g of DI water generating 0.46 M solution of KOH, which was used in the following procedure for zeolite synthesis. In general, 0.27 g of $C_9H_{21}AIO_3$ was dissolved in 10.0 g of aqueous KOH solution, producing solution A. Solution B was prepared by addition of 5.49 g of TEOS into 15.60 g of aqueous KOH solution under vigorous stirring. Separately, 0.48 g of CTAB and 9.0 g of silicalite-1 seed-sol were added subsequently to 10 g of KOH solution, generating solution C. After $C_9H_{21}AIO_3$ and TEOS were fully dissolved, solution A was slowly added dropwise into solution B, and stirred at room temperature for 5 h. Then, solution C was added. The molar composition of the resultant mixture was 40TEOS: $1Al_2O_3$: 25KOH: $3000H_2O$: 2CTAB. After stirring for 1 h, the obtained gel was heated at 448 K for 12-96 h under autogenous pressure and static conditions in a Teflon-lined stainless-steel autoclave. The resulting solid was washed repeatedly with DI water until pH 7 was obtained, then dried at 393 K for 12 h, and calcined at 823 K for 5 h in air flow (30 mL min⁻¹). For acquisition of H⁺ form ZSM-5, the calcined samples were ion-exchanged with 1.0 M NH₄Cl solution (weight ratio of zeolite to NH₄Cl solution = 1:20) at 353 K for 2 h, followed by centrifugation and washing with DI water. This process was repeated three times and then calcined at 823 K under air flow (30 mL min⁻¹) for 5 h. The obtained samples are denoted as CMZS. S1.4 Material characterization

X-ray diffraction (XRD) patterns were collected using D8 A25 DaVinci X-ray diffractometer (Bruker) with (Cu $K\alpha$, $\lambda = 1.541$ Å) radiation. Scanning electron microscopy (SEM) was acquired via Regulus 8100 (Hitachi) instrument operating at 5 kV with a gold (30 s) metal coating. Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), selected area electron diffraction (SAED), and high-angle annular dark-field STEM (HAADF-STEM) were recorded using Tecnai G2 F30 (Philips) instrument operating at 300 kV. N₂ adsorption/desorption analysis was performed by ASAP 2460 (Micromeritics) instrument at 77 K. Before the test, all samples were degassed at 573 K under N₂ flow for 3 h. The mesopore surface area was calculated by Brunauer-Emmett-Teller method. The mesopore volume and mesopore size were determined according to the Barrett-Joyner-Halenda (BJH) procedure using the adsorption isotherms. Total pore volumes were calculated from the amount of N_2 adsorbed at a relative pressure p/p_0 of 0.99. Temperature programmed desorption of ammonia (NH₃-TPD) was registered by DAS-7200 (Hunan Huasi) instrument equipped with a thermal conductive detector (TCD). Thermo gravimetric-analysis (TGA) was performed using STA S16 (Setaram) instrument under air flow of 20 mL min⁻¹ at a heating rate of 10 °C/min. FT-IR spectroscopy was carried out with FT-IR S2 (Perkin) in a resolution of 2 cm⁻¹. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was conducted by Optima 7000DV (Perkin) using a nonmonochromatic Mg Ka excitation source at 15 kV. Solid-state nuclear magnetic resonance (NMR) spectra were recorded on AVANCE III 600 (Agilent). S1.5 Computational methods

The calculations were carried out based on the density functional theory (DFT) using Vienna Ab initio Software Package (VASP 5.3.5) code within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation. The projected augmented wave (PAW) method was applied to describe the core-electron interactions and plane-wave basis of the cutoff energy was set to 400 eV. Monkhorst-Pack (MP) grids were utilized to analyze the Brillouin zone of the zeolite and surface unit cell, with Γ k-point mesh for optimizations. The convergence criterion of the electronic selfconsistent iteration and force was fixed at 10⁻⁵ eV and 0.01 eV/Å, respectively. The calculated lattice constants were a=19.6Å, b=20.0Å, c=13.5Å, and $\alpha = \beta = \gamma = 90^{\circ}$, which was in accordance with the conventional MFI structure. S1.6 Catalysis tests MTO reaction was conducted at 480 °C in a stainless-steel fixed bed reactor under atmospheric pressure. The catalyst (1.0 g, 20-40 mesh) was loaded in the stainless-steel reactor (8 mm inner diameter). The liquid feed stream (n (H₂O): n(methanol) =1.23) was pumped into the reactor at a flow of 0.12 mL min⁻¹ using a syringe pump with N₂ as the carrier gas (20 mL min⁻¹), which gave WHSV of 1 h⁻¹. The gaseous fraction was analyzed on-line by a gas chromatograph (ZHONGKE HUIFEN GC-7820), fitted with a flame ionization detector (FID) and GC columns (RESTEK, Rt-Q-BOND, 30 m × 320 µm × 10 µm). The area normalization method with relative molar correction factor was adopted. According to correction factor f of each substance, the area percentage content in GC was converted to molar percentage content. Methanol conversion was defined as the molar ratio of converted methanol vs methanol of the reactor's inlet. Selectivity of hydrocarbons was defined as the molar ratio of ethylene and propylene, which was generated in MTO reaction vs the total amount of hydrocarbon. Both methanol and dimethyl ether (DME) were regarded as reactants for the calculation.

S2. Results and discussion

Silicalite-1 seed sol Synthesis and Characterization. As displayed in Fig. S1, Silicalite-1 seed sol showed a typical Tyndall effect, indicating that the diameter of colloidal particles was between 1 and 100 nm. Moreover, Silicalite-1 seed consisted of spherical nanoparticles with the sizes of 10-150 nm and presents the characteristic peaks of MFI-type zeolite, as shown in Fig. S2. Fig. S3 displays the size distribution for the colloidal particles in Silicalite-1 seed sol under study at 25 °C. Three peak distributions were discovered at 1-2 nm, 10–13 nm and 14-120 nm and reached a maximum at 11 nm and 105 nm, where nearly all particles in the seed sol have a diameter between 10 nm to 120 nm, which was consistent with SEM results.



Fig. S1 Optical photograph and SEM image of silicalite-1 seed sol



Fig. S2 XRD patterns of silicalite-1 seed sol



Fig. S3 size distribution of silicalite-1 seed sol

CMZS Synthesis and Characterization.



Fig. S4 Optical photograph of CMZS

The density of the sponge monoliths (0.3261 g/cm^3) is less than water, so it floating on the surface of the water, or even standing on the dandelion.



Fig. S5 XRD patterns of CMZS and CZSM-5

Sample	FWHM			
2-Theta/°	CZSM-5	CMZS		
7.9	0.108	0.134		
8.9	0.161	0.208		
9.1	0.098	0.198		
23.1	0.172	0.369		
23.7	0.115	0.217		
23.9	0.103	0.161		
24.43	0.096	0.129		

Table S1. Peak position and FWHM of CMZS and CZSM-5



Fig. S6 N₂ adsorption-desorption isotherms and BJH pore size distributions of CMZS

Table S2. Textural properties of CMZS

sample	SiO ₂ /Al ₂ O ₃	$\frac{S_{micro}}{[m^2 g^{-1}]}$	$\frac{S_{ext}}{[m^2 g^{-1}]}$	$\frac{V_{micro}{}^{a}}{\left[cm^{3}{}g^{\text{-}1}\right]}$	$\begin{array}{c} V_{total}{}^{b} \\ [cm^{3} g^{\text{-1}}] \end{array}$	V _{meso} ^c [cm ³ g ⁻¹]	${S_{BET}}^{d}$ [m ² g ⁻¹]
CMZS	28.16	168.6341	106.5852	0.0851	0.1745	0.0894	275.2193

^a Determined from t-plot method; ^b Determined by non-localized density functional theory (NLDFT) method from adsorption branch of N₂ isotherm at $P/P_0 = 0.99$; ^c V_{meso} = Vt - V_{micro}; ^d Determined from Brunauer, Emmett, and Teller (BET) method; SiO₂/Al₂O₃ molar ratio of the sample determined by ICP analysis



Fig. S7 Optical photograph of CMZS samples crystallized for different time



Fig. S8 SEM images of CMZS samples crystallized for different time



Fig. S9 XRD patterns of CMZS samples crystallized for different time



Fig. S10 SEM images of samples crystallized without Silicalite-1 seed or CTAB for 96h



Fig. S11 XRD patterns of samples crystallized without Silicalite-1 seed or CTAB for 96h



Fig. S12 SEM image of samples crystallized with 8% TPAOH for 96h



Fig. S13 XRD pattern of samples crystallized with 8% TPAOH for 96h



Fig. S14 SEM image of CZSM-5 (Nankai University $(SiO_2/Al_2O_3 = 36)$ in the NH₄⁺-form)



Fig. S15 MH₃-TPD profiles of CMZS and CZSM-5

The amount and strength of acid sites of CZSM-5 and CMZS zeolites were investigated by using NH_3 -TPD technique. As seen, the profiles exhibit two well resolved desorption peaks in the region below 600 °C. The high temperature peak (300- 500 °C) is attributed to NH_3 eluted from strong acid sites, while the low temperature peak (100- 280 °C) is assigned to the weak acid sites. In addition, this peak area allows an estimation for the amount of acid sites with the assumption of one NH_3 molecule per acid site. Table S3 presents a comparison of the amount and strength of acid sites for CZSM-5 and CMZS zeolites.

Table S3. NH₃-TPD acidity of zeolite samples

sample	Peak temperature/°C		Acidity amount/mmol.g ⁻¹		
	Weak acidity	Strong acidity	Weak acidity	Strong acidity	Total acidity
CZSM-5	186	406	0.15	0.09	0.24
CMZS	178	423	0.18	0.12	0.30



Figure S16. MTO catalytic activity of CZSM-5



Fig. S17 MTO catalytic activity of CMZS