

## Supporting Information

### **Anisotropic ZSM-5 Nanorod Assemblies: Facile Synthesis, Epitaxial Growth, and Strikingly Enhanced Stability in Benzene Alkylation**

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## 1. Experimental Section

### 1.1 Materials

The following chemicals were used as reagents for silicalite-1 (Sil-1) seed synthesis: tetraethyl orthosilicalite (TEOS, AR, Tianjin Kemiou Chemical Reagent Co. Ltd.), tetrapropylammonium hydroxide (TPAOH, 25 wt% in water, Zhejiang Kente Chemical Reagent Co. Ltd.), ethanol (EtOH, AR, Sinopharm Chemical Reagents Co. Ltd.), and deionized water. The following chemicals were used for zeolite ZSM-5 synthesis: colloidal silica (30 wt.% in water, Qingdao Chengyu Chemical Reagent Co. Ltd.), sodium aluminate ( $\text{NaAlO}_2$ , AR, Sinopharm Chemical Reagents Co. Ltd.), sodium hydroxide (NaOH, AR, Sinopharm Chemical Reagents Co. Ltd.), cetyltrimethylammonium bromide (CTAB, AR, Sinopharm Chemical Reagents Co. Ltd.), and deionized water. In addition, for comparison, commercial ZSM-5 (denoted as NK-ZSM-5) was purchased from the catalyst plant of Nankai University.

### 1.2 Synthesis of MFI zeolites

#### 1.2.1 Synthesis of Sil-1 Seed suspension

Sil-1 seed suspension was prepared using the solution mixture with the composition of  $1\text{SiO}_2: 0.35\text{TPAOH}: 14.4\text{H}_2\text{O}: 7.9\text{EtOH}$ . First, 29.6 g of TPAOH, 23.6 mL of EtOH and 4 mL of deionized water were mixed and stirred for 20 min at room temperature. Then, 23.1 mL of TEOS was added dropwise to the above solution and homogenized overnight. Finally, the mixture was transferred to a Teflon-lined steel autoclave and hydrothermally treated at 120 °C for 48 h. After that, the resulting sil-1 suspension was used directly as seeds for subsequent zeolite induced synthesis without any further treatment including separation and washing steps repeatedly.

#### 1.2.2 Preparation of ZSM-5 Nanorod Assemblies

The synthesis of ZSM-5 nanorod assemblies and the effect of CTAB on their formation were investigated using the following molar composition of  $1\text{SiO}_2: 0.033\text{Al}_2\text{O}_3: 0.21\text{Na}_2\text{O}: x\text{CTAB}: 50\text{H}_2\text{O}$  with 1 wt.% Sil-1 seed suspension ( $x=0.005-0.04$ ). In a typical experiment with a molar composition of  $1\text{SiO}_2: 0.033\text{Al}_2\text{O}_3:$

0.21Na<sub>2</sub>O: 0.005CTAB: 50H<sub>2</sub>O, 0.25 g of NaAlO<sub>2</sub>, 0.26 g of NaOH, 0.083 g of CTAB, and 32.14 g of H<sub>2</sub>O were first mixed at room temperature to prepare solution A. Then, 9.16 g of 30 wt.% silica sol was added slowly into the obtained mixture to produce solution B. After 30 minutes of stirring, 0.255 mL of the sonicated seed suspension (1 wt.%, based on the total SiO<sub>2</sub> in the synthesis gel) with the crystal size of ca. 188 nm was added dropwise into the above solution B and aged at room temperature for 3 h. Finally, the obtained gel was transferred into the autoclave and crystallized at 170 °C for 24 h under a static condition. After hydrothermal treatment, the solid products were filtered and washed with deionized water several times and then dried at 80 °C overnight, followed by calcination in air at 550 °C for 6 h. The samples synthesized under different conditions are denoted as NA-ZSM-5<sub>x</sub>, where NA represents the nanorod assemblies, and X represents the CTAB content.

Following a similar procedure, the crystallization process was carried out by synthesizing a series of samples with different crystallization times (1.5 h, 3.5 h, 8 h, 12 h, 16 h, and 24 h) using the gel compositions of 1SiO<sub>2</sub>: 0.033Al<sub>2</sub>O<sub>3</sub>: 0.21Na<sub>2</sub>O: 0.005CTAB: 50H<sub>2</sub>O with 1 wt.% Sil-1 seed suspension.

For comparison, the conventional ZSM-5 (C-ZSM-5) with a typical hexagonal prism morphology was prepared from the gel with a composition similar to the above-mentioned NA-ZSM-5 sample but using TEOS as the silica source and without CTAB.

### **1.2.3 Preparation of H-ZSM-5 Catalysts**

H-ZSM-5 catalysts were obtained by NH<sub>4</sub><sup>+</sup> ion exchange of the synthesized samples. Typically, 1 g of the obtained sample was impregnated with 10 mL of 1.0 M NH<sub>4</sub>NO<sub>3</sub> aqueous solution under stirring at 80 °C for 2 h. This procedure was repeated three times, followed by drying and calcination at 550 °C in the air for 6 h. The achieved HZSM-5 samples were directly used in the catalytic test without any modification after being pressed into pellets and crushed into 20–40 mesh particles, respectively.

## **1.3 Characterizations**

The morphologies and crystal sizes were determined by scanning electron microscopy (SEM, FEI Nova NanoSEM 450) and transmission electron microscopy

(TEM, FEI Tecnai G2F30 and JEOL JEM-F200). The crystalline structure of the zeolite samples was recorded by X-ray diffraction (XRD) on a Rigaku SmartLab diffractometer. The relative crystallinity was calculated by comparing the diffraction intensities of five typical characteristic peaks of MFI zeolite ( $2\theta = 7.9, 8.9, 23.0, 23.9,$  and  $24.4^\circ$ ) to the product with the highest intensity.  $N_2$  adsorption-desorption isotherms were performed on an Autosorb-iQ-C gas adsorption analyzer (Quantachrome). Acid amount and strength were measured by temperature-programmed desorption of ammonia ( $NH_3$ -TPD) on a CHEMBET-3000 automatic chemical adsorption instrument (Quantachrome). The silanol groups of the achieved zeolite samples were measured by a Fourier transform infrared (FTIR) spectroscopy using a Bruker EQUIOX-55 instrument. The  $SiO_2/Al_2O_3$  ratio of the samples was analyzed by X-ray fluorescence (XRF) spectroscopy using a Bruker SRS-3400 instrument. The  $^{27}Al$  and  $^{29}Si$  MAS NMR experiments were recorded on an Agilent DD2-500 spectrometer. The coke content of spent catalysts was measured using a TG/SDTA 851E instrument.

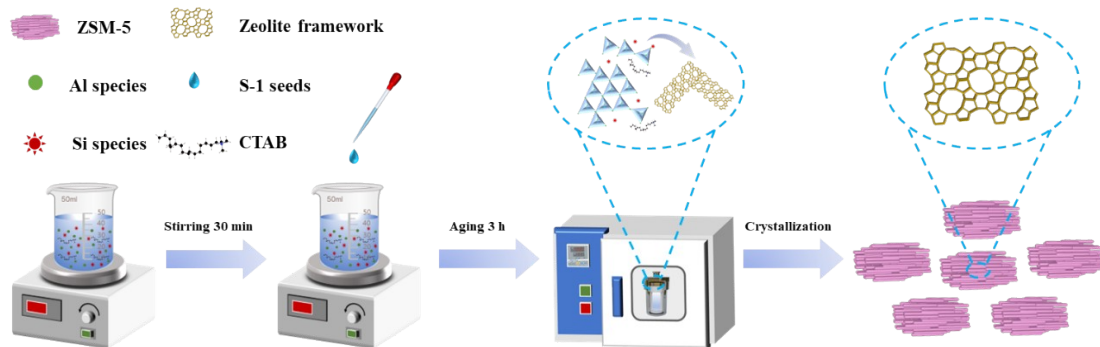
#### 1.4 Catalytic Performance Evaluation

The alkylation of benzene with ethanol was conducted in a fixed-bed stainless reactor (12 mm i.d.) at atmospheric pressure. In a typical experiment, 1.0 g of catalyst (20–40 mesh) was placed in a constant temperature section of the reactor, and both two sides were filled with quartz sand. Before starting each reaction, the catalyst was preheated at  $370^\circ C$  under  $N_2$  flow (30 mL/min) for 2 h, and then the temperature was adjusted to the reaction temperature of  $350^\circ C$ . A mixture of benzene and ethanol (molar ratio of 4/1 or 2/1) was introduced into the reactor using an LC-10P high-pressure low-pulsation infusion pump with a weight hourly space velocity (WHSV) of  $6\ h^{-1}$ . The products were analyzed by a gas chromatograph (GC7900, TIANMEI Co., Ltd.) equipped with a FID detector and a SE-30 capillary column ( $60\ m \times 0.32\ mm \times 1.0\ \mu m$ ). The benzene conversion (X) and the product selectivity ( $S_i$ ) were calculated using the following equation:

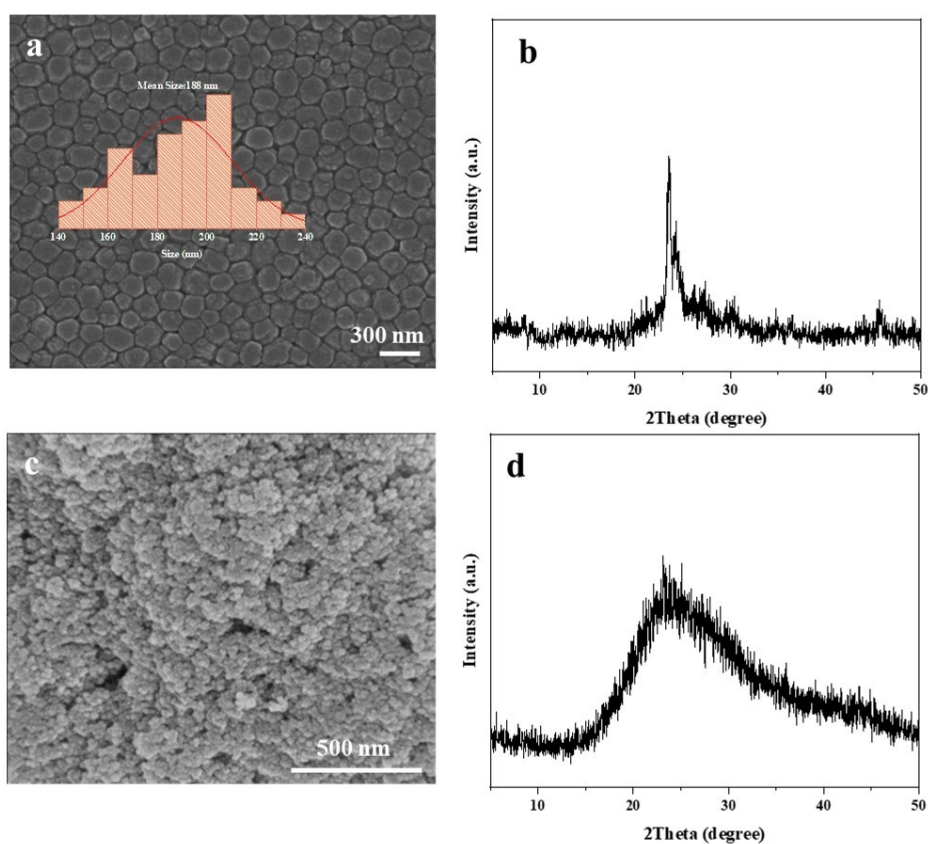
$$X_{\text{benzene}} (\%) = \frac{\text{moles of benzene in} - \text{moles of benzene out}}{\text{moles of benzene in}} \times 100\%$$

$$S_i (\%) = \frac{\text{moles of desired product } i}{\text{moles of consumed benzene}} \times 100\%$$

Where the “i” is the aromatic product. The target aromatic product is alkylbenzene including ethylbenzene and diethylbenzene.



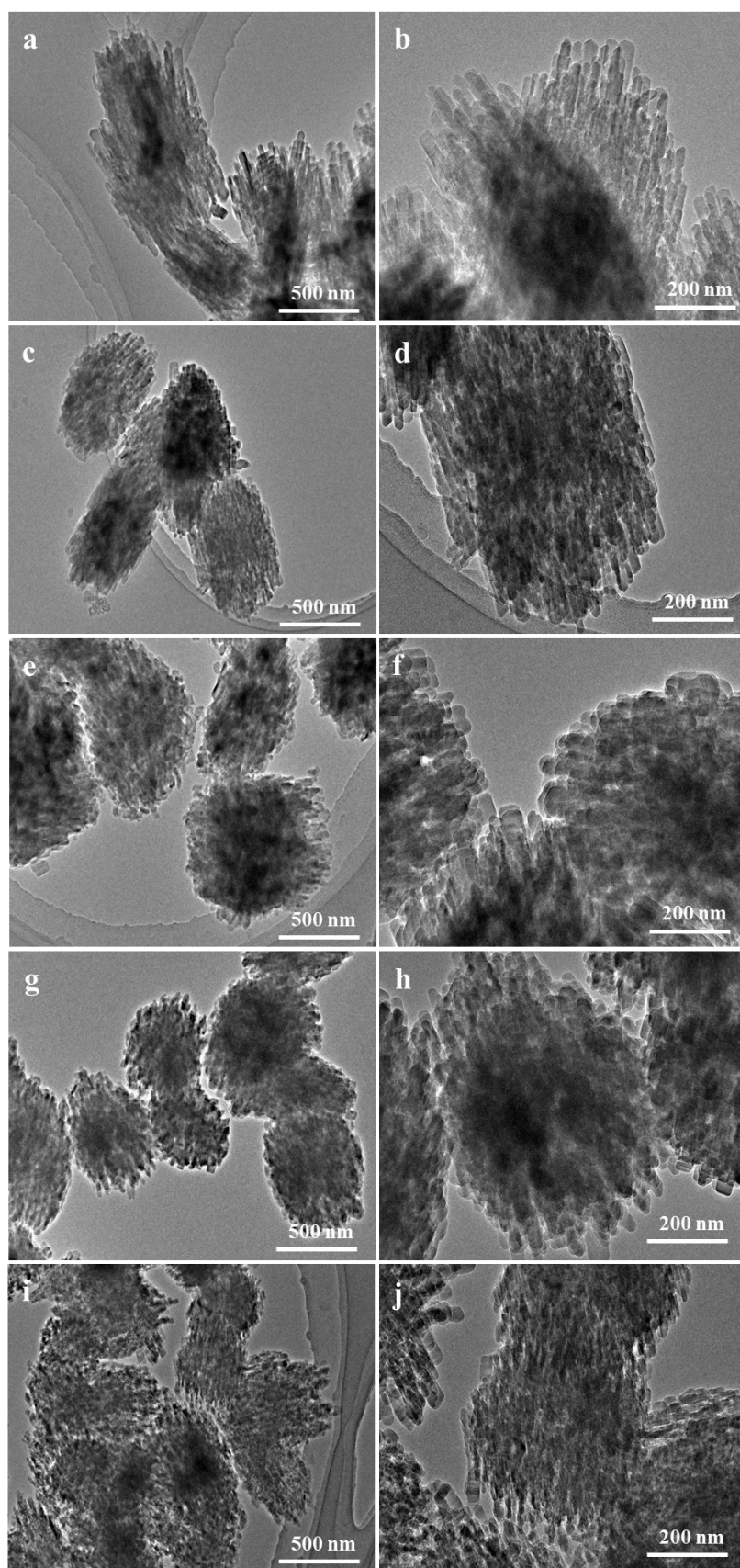
**Scheme S1.** Schematic illustration of the synthesis route for ZSM-5 nanorod assemblies.



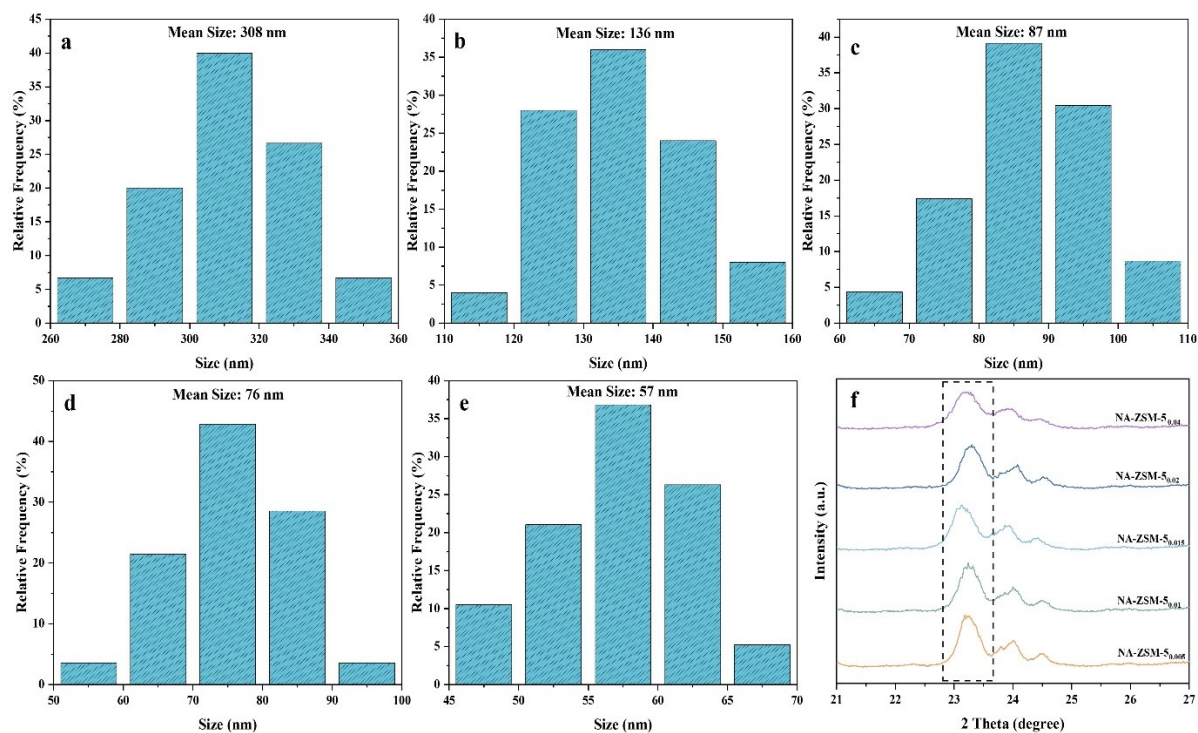
**Fig. S1** SEM images and XRD patterns of different samples: (a-b) the sil-1 seed suspension; (c-d) the synthesized samples without adding any sil-1 seed suspension.

**Note:** As shown in **Fig. S1**, the seeds are spheroidal particles with the size of about 188 nm. XRD pattern confirms that the seed crystals possess relatively low crystallinity.

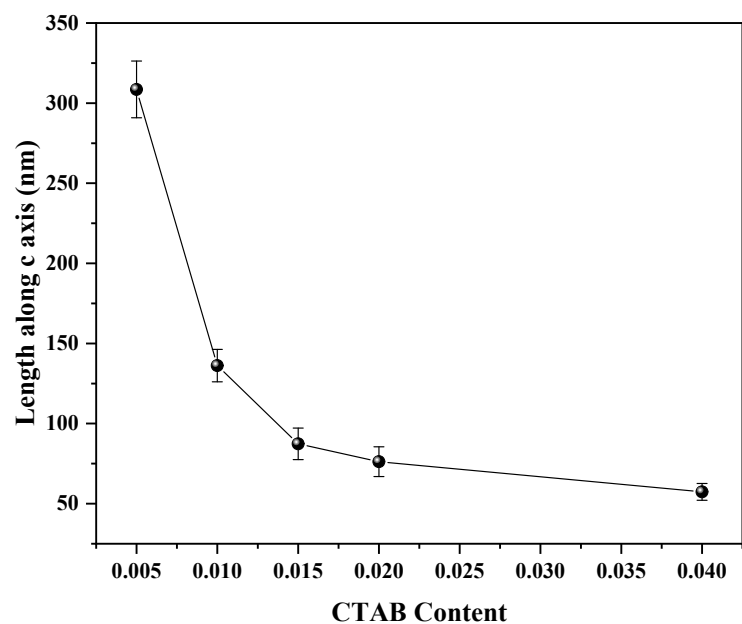




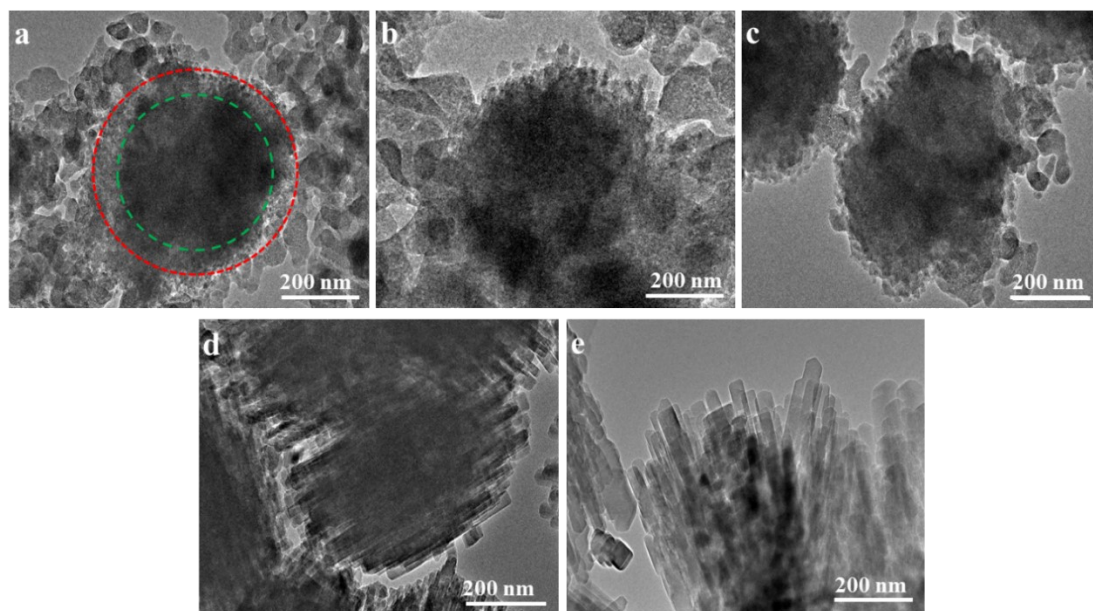
**Fig. S2** TEM images of solid products synthesized from the system  $1\text{SiO}_2: 0.033\text{Al}_2\text{O}_3: 0.21\text{Na}_2\text{O}: x\text{CTAB}: 50\text{H}_2\text{O}: 1 \text{ wt.\% silicate-1 seed suspension}$ , where  $x$  is 0.005 (a, b), 0.01 (c, d), 0.015 (e, f), 0.02 (g, h), 0.04 (i, j).



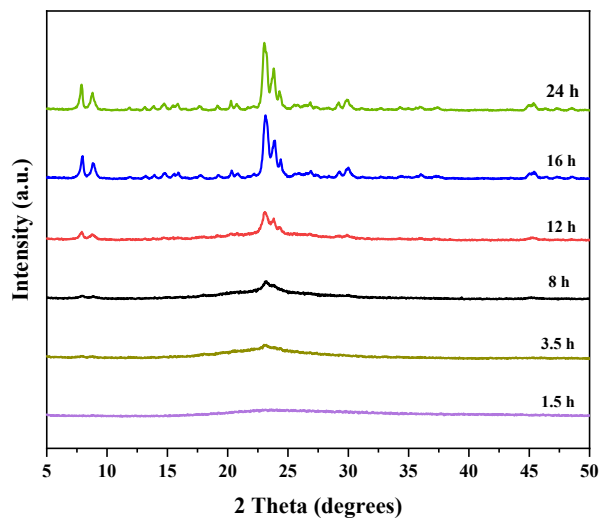
**Fig. S3** Nanorod length size distribution and XRD patterns of solid products synthesized from the system  $1\text{SiO}_2: 0.033\text{Al}_2\text{O}_3: 0.21\text{Na}_2\text{O}: x\text{CTAB}: 50\text{H}_2\text{O}: 1 \text{ wt.}\% \text{ silicate-1 seed suspension}$ , where  $x$  is 0.005 (a), 0.01 (b), 0.015 (c), 0.02 (d), 0.04 (e). Note: Nanorod length size of the samples was measured in SEM and TEM images by averaging more than 50 crystal particles.



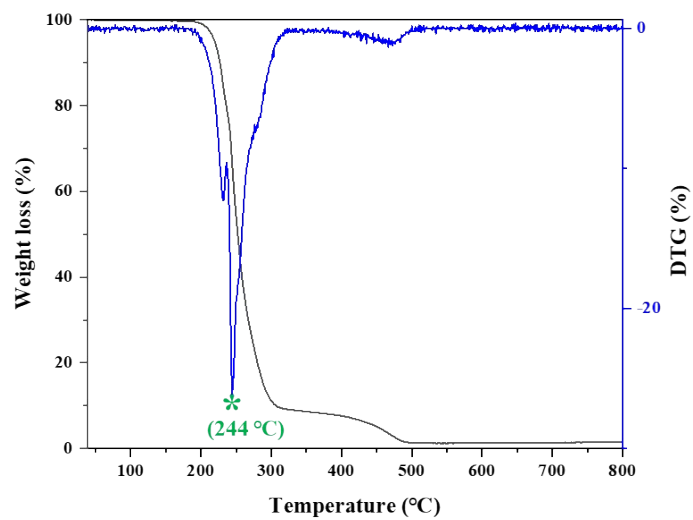
**Fig. S4** The length size distribution along the c-axis of nanorod crystals of solid products synthesized with different CTAB content.



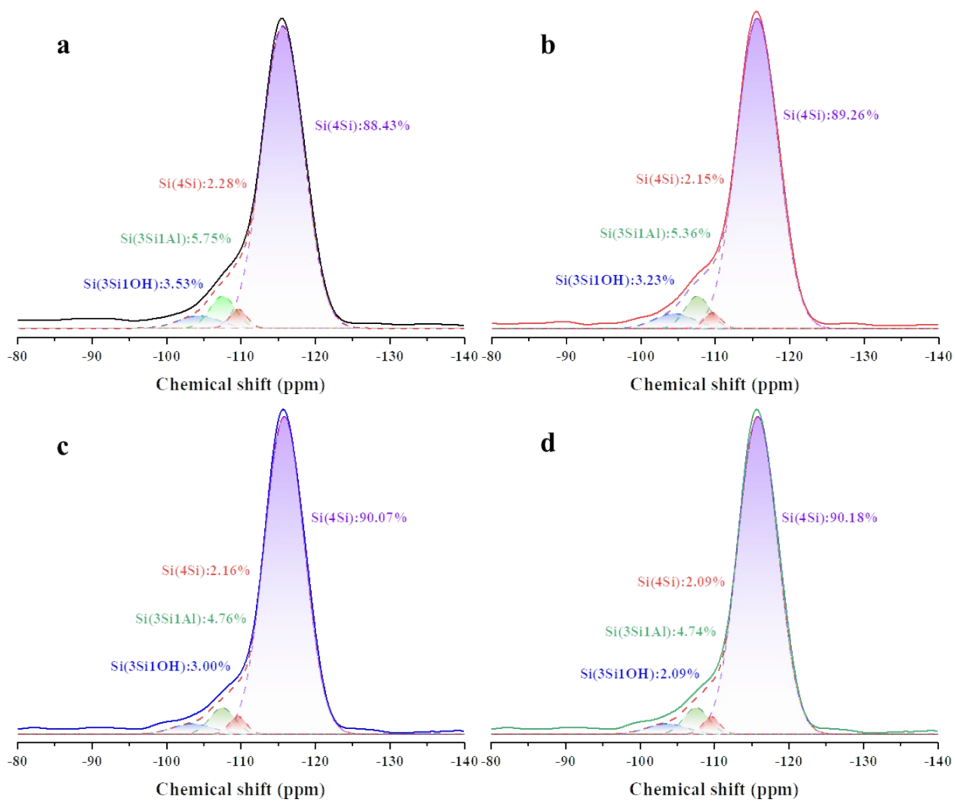
**Fig. S5** TEM images of intermediates crystallized at different crystallization time: 3.5 h (a); 8 h (b); 12 h (c); 16 h (d); 24 h (e). The green and the red lines represent the outer boundary of the seed and its outer precursor layer, respectively.



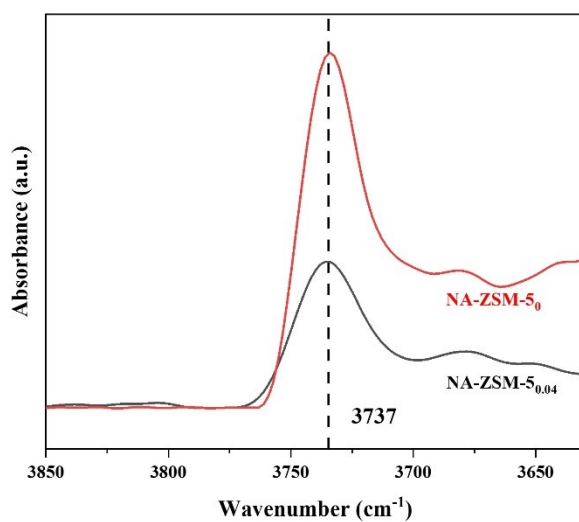
**Fig. S6** XRD patterns of ZSM-5 nanorod assemblies at different crystallization time.



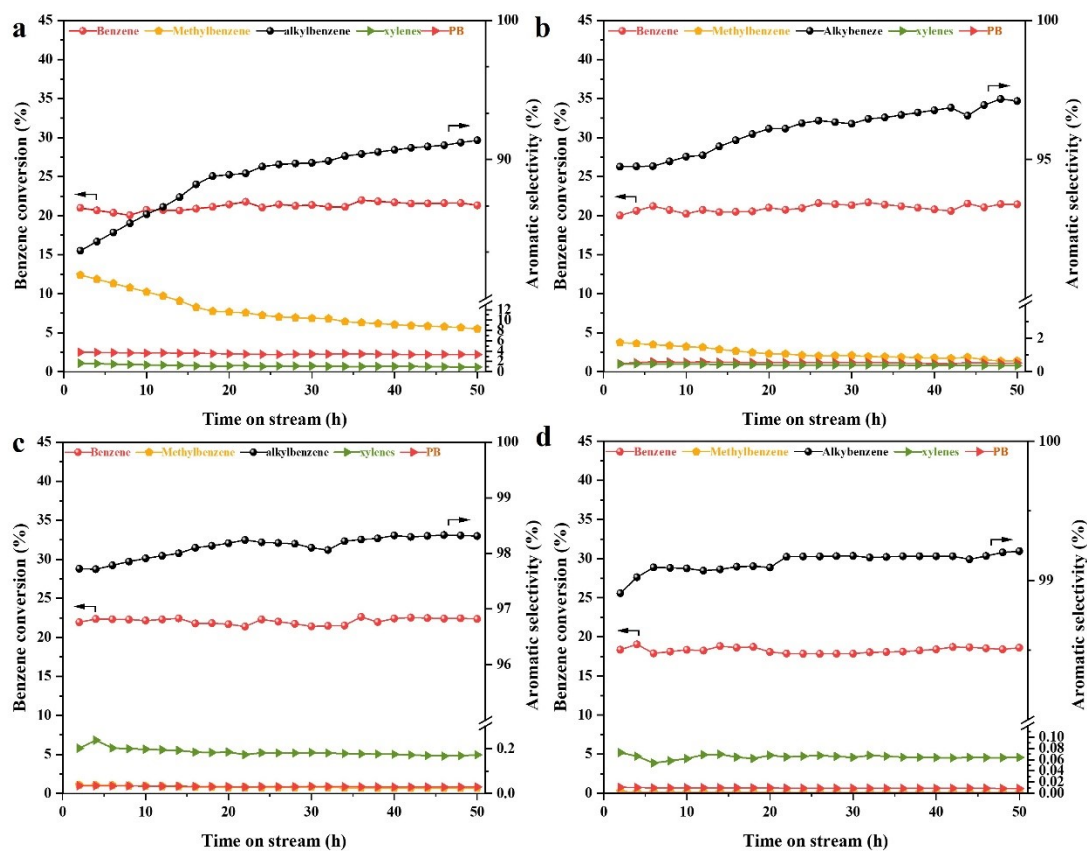
**Fig. S7** TG and DTG curves of pure CTAB.



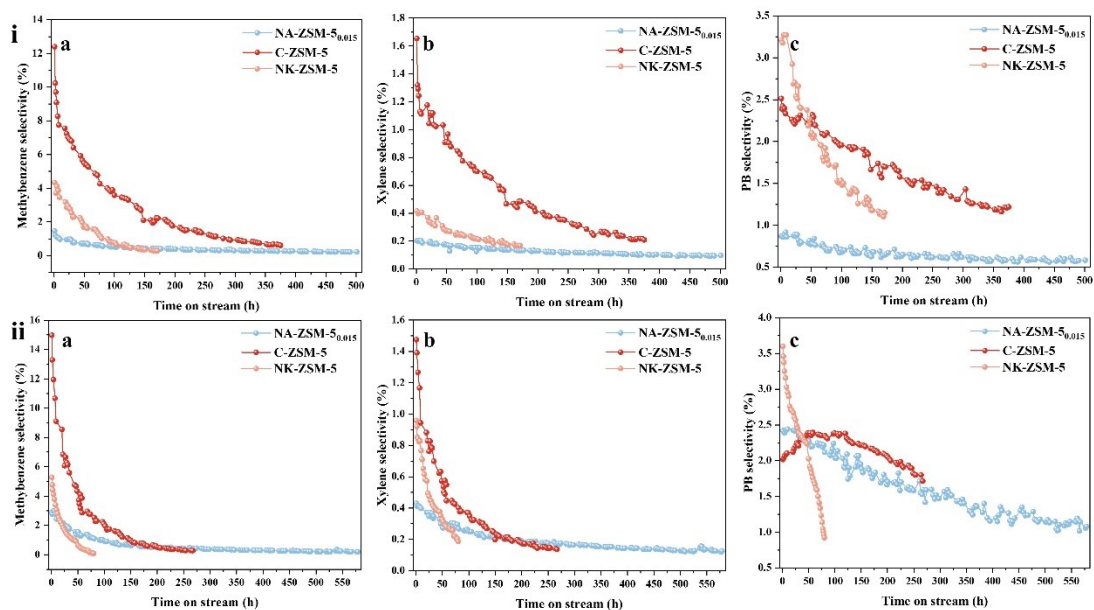
**Fig. S8**  $^{29}\text{Si}$  MAS NMR spectra of NA-ZSM-5<sub>0.005</sub> (a), NA-ZSM-5<sub>0.01</sub> (b), NA-ZSM-5<sub>0.015</sub> (c) and NA-ZSM-5<sub>0.02</sub> (d). **Note:** all the samples are uncalcined.



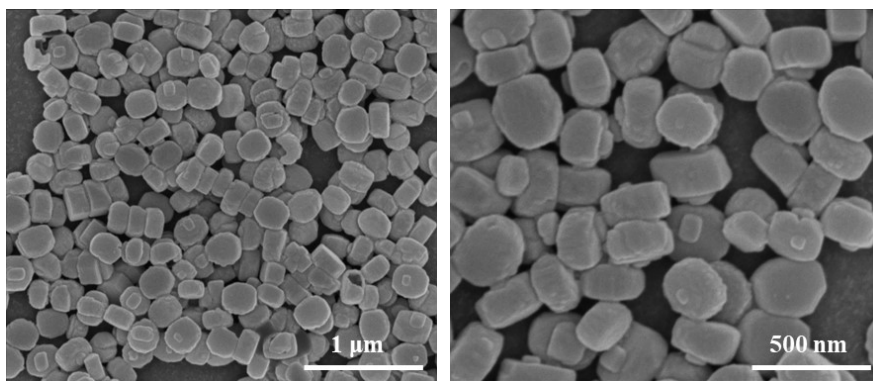
**Fig. S9** OH-IR spectra of NA-ZSM-5<sub>0.04</sub> and NA-ZSM-5<sub>0</sub>. **Note:** all the samples are uncalcined.



**Fig. S10** Dependence of catalytic conversion and product selectivity on the reaction time over C-ZSM-5 (a), NA-ZSM-5<sub>0.005</sub> (b), NA-ZSM-5<sub>0.015</sub> (c), NA-ZSM-5<sub>0.02</sub> (d). Reaction conditions: 1.0 g catalyst, 350 °C, WHSV= 6 h<sup>-1</sup>, atmospheric pressure, molar ratio of benzene to ethanol is 4.



**Fig. S11** Long-term reaction stability of benzene alkylation with ethanol with time over three samples under different molar ratios of benzene to ethanol: (i) 4; (ii) 2; (a) methylbenzene selectivity; (b) xylene selectivity; (c) PB selectivity. Reaction conditions: 1.0 g catalyst, 350 °C, WHSV= 6 h<sup>-1</sup>, atmospheric pressure. Note: the catalytic lifetime is defined as the benzene conversion drops to 90% of initial data and the reaction end is set as the conversion falls below ~80% of initial data.



**Fig. S12** SEM images of conventional C-ZSM-5 zeolites.

**Table S1** Relative peak areas of  $^{29}\text{Si}$  MAS NMR spectra for different samples.

Sample	Chemical shift ( $\delta$ , ppm) and distribution of Si environments (% in brackets)		
	Q4(4Si)	Q4(3Si1Al)	Q3(3Si1OH)
NA-ZSM-5 <sub>0</sub>	-115, -110 (89.25%)	-107 (6.71%)	-102 (4.04%)
NA-ZSM-5 <sub>0.04</sub>	-115, -110 (92.58%)	-107 (4.54%)	-102 (2.88%)

**Table S2** Benzene conversion and aromatic selectivity over NA-ZSM-5<sub>0.015</sub> and conventional ZSM-5 samples **under high benzene to ethanol of 4** <sup>a</sup>.

Samples	Conversion <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)				Lifetime <sup>c</sup> (h)
		Alkylbenzene	Methylbenzene	Xylene	PB	
NA-ZSM-5 <sub>0.015</sub>	22.3	98.7	0.5	0.1	0.7	>500
C-ZSM-5	19.5	92.8	4.4	0.8	2.0	220
NK-ZSM-5	18.3	95.4	2.1	0.3	2.2	99

<sup>a</sup> Data are collected and calculated based on mass weight; <sup>b</sup> the average values before the conversion of ethanol was less than 90%; <sup>c</sup> lifetime until the reaction decreased to ~90% of initial benzene conversion; and <sup>e</sup> product content is undetectable or almost negligible. Reaction conditions: 1.0 g catalyst, 350 °C, WHSV= 6 h<sup>-1</sup>, atmospheric pressure, **molar ratio of benzene to ethanol is 4**.

**Table S3** Benzene conversion and aromatic selectivity over NA-ZSM-5<sub>0.015</sub> and conventional ZSM-5 samples **under high benzene to ethanol of 2** <sup>a</sup>.

Samples	Conversion <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)				Lifetime <sup>c</sup> (h)
		Alkylbenzene	Methylbenzene	Xylene	PB	
NA-ZSM-5 <sub>0.015</sub>	38.1	97.0	0.9	0.2	1.9	370
C-ZSM-5	35.8	91.0	6.0	0.7	2.3	81
NK-ZSM-5	34.6	94.4	2.3	0.6	2.8	49

<sup>a</sup> Data are collected and calculated based on mass weight; <sup>b</sup> the average values before the conversion of ethanol was less than 90%; <sup>c</sup> lifetime until the reaction decreased to ~90% of initial benzene conversion; and <sup>e</sup> product content is undetectable or almost negligible. Reaction conditions: 1.0 g catalyst, 350 °C, WHSV= 6 h<sup>-1</sup>, atmospheric pressure, **molar ratio of benzene to ethanol is 2**.



**Table S4** Alkylation performance of benzene with ethanol over ZSM-5 zeolites in literature.

Samples	Condition			Catalytic performance			Reference
	Temperature (°C)	B/E <sup>a</sup>	WHSV (h <sup>-1</sup> )	Conversion (%)	Alkylbenzene selectivity (%)	TOS (h)	
1%MgO-AT-ZSM-5	385	2	4	20.6	92	100	48
2.6%ZnO-ZSM-5	380	4	4	21.9	89.9	-	49
Hierarchical ZSM-5	350	2	7.5	32	92	25	51
Hierarchical ZSM-5	350	2	3	35.8	96.2	36	52
5%MgO-4%B-ZSM-5	350	2	3.26	34.49	85.5	-	53
3%La <sub>2</sub> O <sub>3</sub> -HZSM-5	354	4	2	24.19	98.8	21	56
NA-ZSM-5 <sub>0.015</sub>	350	4	6	22.3	98.1	500	This work
NA-ZSM-5 <sub>0.015</sub>	350	2	6	38.1	97.0	579	This work

<sup>a</sup> B/E represents the molar ratio of benzene to ethanol.

**Table S5** Coke content and coking rate over spent samples.

Samples	TOS (h)	Coke content <sup>a</sup> (mg.g <sub>cat</sub> <sup>-1</sup> )	Coking rate <sup>b</sup> (mg.g <sub>cat</sub> <sup>-1</sup> .h <sup>-1</sup> )
NA-ZSM-5 <sub>0.015</sub>	579	74.1	0.13
C-ZSM-5	267	88.5	0.33
NK-ZSM-5	79	96.0	1.22

<sup>a</sup> Calculated by weight loss in TG curves; <sup>b</sup> Calculated by the ratio of coke content to TOS.