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Supplementary Information:

Seed-induced synthesis of hierarchical ZSM-5 nanosheets in the

presence of hexadecyl trimethyl ammonium bromide

Min Liu, Junhui Li, Wenzhi Jia, Mengjiao Qin, Yanan Wang, Kai Tong, Huanhui Chen and

Zhirong Zhu*

Department of Chemistry, Tongji University, Shanghai 200092, China.

To whom correspondence should be addressed. E-mail: zhuzhirong@tongji.edu.cn

Experimental Section

1. Preparation

Hierarchical ZSM-5 (Hi-ZSM-5). Seed-induced synthesis of Hi-ZSM-5 nanosheets was carried out from a starting aluminosilicate gel at temperature of 443 K in the presence of calcined ZSM-5 zeolite seeds. As a typical run for synthesis of Hi-ZSM-5 at 443 K, (1) 1.34 g of aluminum sulfate ($Al_2(SO_4)_3$) and 2.38 g of sodium chloride (NaCl) were dissolved in 35.00 ml of deionized water, followed by addition of 1.12 g of sulfuric acid (H_2SO_4 , 98 wt.%), the result transparent solution was labeled A; (2) Solution A and 22.50 g of sodium silicate (Na_2SiO_3) solution were added dropwise and simultaneously into 30 ml deionized water under continous stirring condition to obtain a gel; (3) After stirring for 10 min, 12.00 ml aqueous ammonia ($NH_3 \cdot H_2O$, 22-25 wt%) and 0.50 g of ZSM-5 seeds (Si/Al=50), were introduced into the gel, followed by addition of 4.75 g tetrapropyl ammonium bromide (TPABr); (4)

The gel mixture was left for 12 h at 363 K for aging, 4.75 g of CTAB was then added; (5) After stirring for 3 h at room temperature, the gel mixture with molar ratio of SiO₂: 0.02Al₂O₃: 0.2NaCl: 0.032H₂SO₄: 1.6NH₃·H₂O: 0.066TPABr: 0.09CTAB: 18.5H₂O was transferred into a stainless-steel autoclave lined with polytetrafluoroethylene (PTFE) to crystallize at 443 K for 48 h under autogeneous pressure; (6) After filtrating at room temperature and drying at about 363 K overnight, crystalline products were obtained.

For comparison, conventional ZSM-5 (C-ZSM-5) zeolite with particle size of 2-3 μ m was synthesized under the similar procedures except for the absence of CTAB, which was designated as 100 % crystallinity.

2. Characterization

X-ray powder diffraction (XRD) patterns of all samples were recorded on a D8-Foucs diffractometer (Bruker) using Cu Ka radiation with an accelerating voltage of 40 kV and a generator current of 40 mA. Infrared spectroscopy (IR) of the samples was recorded by a Nicolet 5700 (Thermo) spectrometer with a resolution of 0.09 cm⁻¹ using a KBr method. Infrared spectroscopy (IR) of the samples was recorded by a Nicolet 5700 (Thermo) spectrometer with a resolution of 0.09 cm⁻¹ using a KBr method. Infrared spectroscopy (IR) of the samples was recorded by a Nicolet 5700 (Thermo) spectrometer with a resolution of 0.09 cm⁻¹ using a KBr method. The acidity of the samples was measured using the method of pyridine adsorption. Scanning electron microscope (SEM) images were obtained on an S-4800 N scanning electron microscope (Hitachi) operating at 3 kV. High-resolution TEM (HR-TEM) pictures were taken on a JEM 2100F microscope with an accelerating voltage of 200 kV. The N₂ adsorption and desorption isotherms at 77 K were measured using a NOVA 2200e. The samples were

outgassed for 3 h at 573 K in N₂ atmosphere before the measurements. Micropore volumes (V_{micro}) and micropore surface areas (S_{micro}) were obtained by the t-plot method. The total pore volumes (V_{tot}) were evaluated at P/P₀ = 0.995. The specific surface areas (S_{BET}) were estimated by the BET method. The pore-size distributions were derived from the desorption branches of the isotherms using Barrett-Joyner-Halenda theory (BJH). Temperature-programmed desorption of ammonia (NH₃-TPD) was performed by using a homemade apparatus PX2000 (Tianjin Pengxiang Technology Limited Corporation). The sample (0.20 g) was pretreated at 773K for 2 h and then cooled down to 393 K under a He flow. Pure NH₃ was injected until adsorption saturation was reached, followed by a flow of He for 1 h. Then the temperature was raised from 393 K to 823 K with a heating rate of 10 K/min and the amount of desorbed ammonia was detected by using thermal conductivity detector (TCD) at 393 K. Elemental composition of the zeolites was determind by inductively coupled plasma optical emission spectroscopy (Varian 720-OES). 15 mg of zeolite powder was placed in a plastic tube. 1.8 mL HCl: HF (70: 30) solution was added to the tube and the suspension was sonicated for 30 min until all of the zeolites were completely dissolved. Then, 0.8 mL of concentrated nitric acid and 8 mL of 5% boric acid solutions were added, and the total volume was adjusted to 10 mL with deionised water.

3. Catalytic tests

All samples used in catalytic tests were H-form. As a typical run, the sample was calcinated at 813 K for 4 h to move the template, then ion-exchanged with 1 mol/L NH₄NO₃ at 363 K, followed by calcination at 813 K for 3 h. This procedure was

repeated for three times. Also, we have selected another one kind of commercial ZSM-5 (Si/Al=50) zeolites as the catalyst for alkylation of toluene with methnol.

Toluene conversions and xylene selectivities were measured in a stainless steel tubular fixed-bed reactor with 1.5 cm inner diameter. The prepared H-form Hi-ZSM-5 catalysts (5.0 g) were activated in flowing hydrogen (30 ml/min) for 2 h at 773 K and cooled to reaction temperature (723 K) before reaction. The feed pulses of reactants (the molar ratio of toluene to methanol is 2.0) were pumped into the reactor by a metering pump. Alkylation was carried out at 1.5 h⁻¹ WHSV under 1.8 MP pressure. The effluent liquid was introduced to the gas chromatograph and analyzed using an HP-PLOT/Al₂O₃ capillary column and a hydrogen flame ionization detector.



Fig. S1 SEM images for C-ZSM-5 zeolites (a) low magnification, (b) high magnification.



Fig. S2 SEM images for ZSM-5 seed samples (a) low magnification, (b) high magnification.



Fig. S3 SEM images for the section of the Hi-ZSM-5 zeolites (a) low magnification, (b) high magnification.



Fig. S4 Different shade HR-TEM images for the Hi-ZSM-5 zeolites (a) and (b).

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Fig. S5 Nitrogen adsorption/desorption isotherms and BJH pore size distribution (inset) curves of Hi-ZSM-5.

	Specific surface area(m ² /g)			Pore volume(cm ³ /g)		
Sample	$\mathbf{S}_{\mathrm{BET}}$	$\mathbf{S}_{\mathrm{micro}}$	S _{ex}	V_{tol}	V _{micro}	V _{meso}
C-ZSM-5	381	329	52	0.18	0.14	0.04
Hi-ZSM-5	397	226	171	0.28	0.11	0.17

Table S1 Textural parameters and catalytic activities for Hi-ZSM-5 and C-ZSM-5 zeolites



Fig. S6 SEM images for precursors after aging (a) 6 h and (b) 12 h.

Fig. S6 shows the images of precursors after aging (a) 6 h and (b) 12 h. After aging 6 h (see Fig. S6 (a)), ZSM-5 seeds partially dissolved into the precursor mixture. The dissolved ZSM-5 seeds as subnanocrystals could induce the induced the primary units [SiO₄] and [AlO₄] into a large amount of subnanocrystals with the help of the structure-directing agent TPABr by the proceeding of aging. After aging 12 h (see Fig. S6 (b)), almost all of the ZSM-5 seeds dissolved and the precursors mixture become abundant in subnanocrystals.



Fig. S7 FT-IR spectrum of Hi-ZSM-5, subnanocrystals and C-ZSM-5.

Fig. S7 shows the FT-IR spectra of subnanocrystals which have the primary structure of MFI zeolites. Specifically (see Fig. S7), the bands in the range at 1100 cm⁻¹ and 450 cm⁻¹ are caused by insensitive internal tetrahedron asymmetric stretching vibrations and bending vibrations. The band at around 800 cm⁻¹ can be attributed to both structure sensitive external tetrahedron and structure insensitive internal tetrahedron symmetric stretching vibrations. Meanwhile, the characteristic band of the double five rings structure of MFI-type zeolites could be observed at 550 cm⁻¹ from all the samples, which can be used to estimated the crystalline degree of the samples. Although the band of the subnanocrystals at 550 cm⁻¹ is weak, it may be indicated that the subnanocrystals could have the primary sturcture of MFI-type zeolites.



Fig. S8 XRD spectrum of subnanocrystals and C-ZSM-5.

Fig. S8 shows the XRD patterns of subnanocrystals and C-ZSM-5. Compared with C-ZSM-5, the subnanocrystals gave a typical pattern of MFI structure (2θ at around 7.8°, 8.9°, 22.5°, 24.0° and 29.8° corresponding to the major peaks of 101, 200, 301, 501, 303 and 503 crystal surfaces), which indicated that the subnanocrystals could have the primary sturcture of MFI-type zeolites.

Reactions	Hi-ZSM-5	C-ZSM-5	ZSM-5	ZSM-5
	(Si/Al=40)	(Si/Al=50)	(Si/Al=40)	(Si/Al=50)
Alkylation of toluene with methanol				
CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	48.2 ^a	41.3 ^a	44.8 ^a	40.4 ^a
toluene o -xylene m -xylene p -xylene	81.7 ^b	65.4 ^b	71.2 ^b	63.8 ^b
$(CH_3)_2 + CH_3OH \longrightarrow (CH_3)_3 + \ge C_9$ xylene trimethylbenzene	7.9 ^c	28.4 ^c	16.3 °	26.5 ^c

Table S2 Catalytic conversion of bulky molecules over Hi-ZSM-5, C-ZSM-5 and commercial ZSM-5 zeolites

Catalyst: 4 g; reaction T=723 K; time=24 h; Toluene: Methanol=2:1 (mol ratio)

a, b and c numbers indicate the percentage toluene conversion, xylene yield and benzene selectivity, repectively.

Cotolyata	Bronsted	acid sites	Lewis acid sites
Catalysis	200 °C	400 °C	200 °C 400 °C
H-ZSM-5/45*	1.27	0.43	0.35 0.12
C-ZSM-5/50*	1.14	0.39	0.29 0.11
C-ZSM-5/45*	1.25	0.42	0.33 0.14

Table S3 Acidity of Hi-ZSM-5, C-ZSM-5 and commercial ZSM-5 (C-ZSM-5/45) zeolites

* indicates the Si/Al ratio estimated by ICP-OES; A relative ratio of Bronsted acid sites to Lewis acid sites was estimated by the corresponding calibrated peak area.



Fig. S9 Toluene conversion over Hi-ZSM-5 and C-ZSM-5 zeolites in the reaction of toluene alkylation with methanol.