Electronic Supplementary Information (ESI)

Supporting Information For

Facile Fabrication of ZSM-5 Zeolite Hollow Spheres for Catalytic Conversion of Methanol to Aromatics

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Experimental Details

Sample preparation

The synthesis gel for the synthesis of ZSM-5 zeolite hollow spheres was prepared according to the following procedures. First, required amounts of sodium aluminate (41 wt.% of Al_2O_3, 41 wt.% of Na_2O, Sinopharm Chem. Reagent Co., Ltd.) and sodium hydroxide (96 wt%, Sinopharm Chem. Reagent Co., Ltd.) were dissolved in deionized water. Then, certain amounts of n-butylamine (NBA, 99 wt.%, Jiangsu Fengyuan Bioengineering Co., Ltd.), ethylenediaminetetraacetic acid disodium salt (Na_2-EDTA) and silica sol (40.5 wt.% of SiO_2, Qingdao Haiyang Chem. Co., Ltd.) were subsequently added and stirred up to formation of a homogeneous gel. The resultant gel has a chemical composition of SiO_2: 0.14 Al_2O_3: 0.09 Na_2O: 31 H_2O: 0.15 NBA: 0.08 Na_2-EDTA. The crystallization was conducted at 170 ^oC for 0 to 38 h in a Teflon-lined autoclave. The solid product was centrifuged, washed, dried and calcined at 550 ^oC for 10 h in air. This is followed by ion-exchanging with aqueous NH_4NO_3 solution (1 M, m(liquid)/m(solid) = 40) for 4 h at 80 ^oC and subsequent calcining at 550 ^oC for 6 h. The obtained sample was designated as ZSM-5-h(*n*) with *n* representing the crystallization time.

For investigation of the crystallization mechanism, the samples were synthesized by adding different amounts of NaCl or Na_2-EDTA (Table S1).

Sample characterization

X-ray powder diffraction (XRD) patterns of as-synthesized samples were recorded on a Rigaku MiniFlex II desktop X-ray diffractometer with monochromated Cu Kα radiation (154.06 pm, 30 kV and 15 mA). Taking the ZSM-5-b4 sample (Table S1) as a reference (it has a crystallinity of 100%), and the relative crystallinity of other samples was estimated by comparing the total area of the peaks at 2θ between 22.5^o and 25^o with that of the reference sample. The scanning electron microscopy (SEM) images to characterize the surface

morphology of sample were taken on a field emission scanning electron microscope (JSM 7001-F, JEOL, Japan). The high-resolution transmission electron microscopy (HRTEM) images of samples were measured on a field emission transmission electron microscope (JEM 2100-F, JEOL, Japan) operating at 200 kV. The ^{29}Si and ^{27}Al MAS NMR spectra were measured on Bruker Avance III 600 MHz Wide Bore spectrometer operating at a magnetic field of 14.2 T. The ^{27}Al MAS NMR spectra were acquired at a spinning rate of 13 kHz with a $\pi/12$ pulse width of 1.0 μs and a recycle delay of 1 s. The ^{29}Si MAS NMR spectra were obtained at a spinning rate of 5 kHz with a $\pi/2$ pulse width of 6 μs and a recycle delay of 20 s.

The amount of silicon and aluminum element in the mother liquid or solid samples of synthesis systems was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Autoscan16, TJA). Nitrogen adsorption/desorption isotherms were measured at -195.8 °C on a TriStar II 3020 gas adsorption analyzer. Prior to the measurement, the zeolite sample was degassed under high vacuum at 300 °C for 8 h. The surface area was calculated from the adsorption branch in the range of relative pressure from 0.05 to 0.25 by Brunauer–Emmett–Teller (BET) method, the micropore volume was calculated from the isotherms by t-Plot method, and total pore volume was estimated in terms of the relative pressure of 0.99. The mesopore volume was obtained from the difference between the total pore volume and micropore volume.

Temperature-programmed desorption of NH_3 (NH_3-TPD) was performed on a Micromeritics AutoChem II 2920 chemisorption analyzer. Approximately 100 mg of zeolite sample was first pretreated at 550 °C for 2 h in an argon stream (30 mL min^{-1}) and then cooled to 120 °C. Saturated adsorption of NH_3 on the zeolite sample was achieved by introducing gaseous NH_3 (5 vol % in argon, 30 mL min^{-1}) into the sample tube for 30 min. After that, the physically adsorbed NH_3 was removed by flushing the sample tube with the argon flow (30 mL min^{-1}) at 120 °C for 2 h. To get the NH_3-TPD profile, the zeolite sample was then heated up from 120 to 550 °C at a ramp of 10 °C min^{-1}; the amount of NH_3 released

during heating for desorption was measured by a thermal conductivity detector (TCD). The quantities of weak and strong acid sites were determined by the amounts of ammonia desorbed at 120−250 and 250−550 °C, respectively.

Pyridine-adsorption infrared (Py-IR) spectrum was measured on a Bruker Tensor 27 FT-IR spectrometer. Before collecting the spectrum, the self-supported sample wafer was evacuated at 450 ^{o}C and 10^{-2} Pa for 2 h, and cooled to room temperature subsequently. Then Pyridine vapor was introduced into the sample cell for 1 h. The spectrum was collected after the sample wafer after evacuation at 150 ^{o}C for 1 h.

Catalyst test

Conversion of methanol to aromatics was carried out in a fixed-bed reactor with an inner diameter of 10 mm. The catalyst was pressed and crushed to 20 – 40 mesh. The reaction conditions are as follows: 1.5 g catalyst, 390 ^{o}C, 0.5 MPa, weight hourly space velocity (WHSV) of methanol of 3.2 h^{-1}. Before the reaction, the catalyst was pretreated at 390 ^{o}C for 10 h in a nitrogen flow (30 mL min^{-1}). The gas and liquid products were separated with a cold trap. The gaseous products were on-line analyzed by an Aglient 7890A gas chromatograph equipped with one thermal conductivity (TCD) and two flame ionization detectors (FID) and two capillary columns (J&W 127-7031, 30 m × 530 μm × 0.25 μm; Agilent 19095P-S25, 50 m × 530 μm × 15 μm). The liquid organic products were analyzed by another Agilent 7890A gas chromatograph equipped with one FID and one capillary column (Agilent 19091S-001, 50 m × 200 μm × 0.5 μm). The aqueous products, including mainly water, methanol and oxygenates, were analyzed by the third Agilent 7890A gas chromatograph equipped with one TCD, one FID and one capillary column (Agilent 19091N-136, 60 m × 250 μm × 0.25 μm).

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□2□Magnified SEM images (a, c, d, e, and f) of (a) ZSM-5-h(22), box 1 in Fig.4c, (c) shell of ZSM-5-h(24), box 2 in Fig. 4d, (d) core of ZSM-5-h(24), box 3 in Fig. 4d, (e) shell of ZSM-5-h(26), box 4 in Fig. 4e, (f) core of ZSM-5-h(26) , box 5 in Fig. 4e; and SEAD pattern of (b) ZSM-5-h(22), red box of shell (Fig.S2);

□3□(A) XRD patterns of the samples synthesized by adding different amounts of NaCl: (a) [NaCl]/[SiO_2] = 0.1, (b) [NaCl]/[SiO_2] = 0.12, (c) [NaCl]/[SiO_2] = 0.16, (d) [NaCl]/[SiO_2] = 0.28 and (e) [NaCl]/[SiO_2] = 0.44; (B) XRD patterns of the samples synthesized by adding different amounts of Na_2-EDTA: (f) [Na_2-EDTA]/[SiO_2] = 0, (g) [Na_2-EDTA]/[SiO_2] = 0.05, (h) [Na_2-EDTA]/[SiO_2] = 0.06, (i) [Na_2-EDTA]/[SiO_2] = 0.08, (j) [Na_2-EDTA]/[SiO_2] = 0.11, (k) [Na_2-EDTA]/[SiO_2] = 0.15; (C) the crystallinities of the samples synthesized by adding different amounts of NaCl; and (D) the crystallinities of the samples synthesized by adding different amounts of Na_2-EDTA (Fig.S3);

□4□(A) Si concentrations, (B) Al concentrations and (C) Si/Al ratios of the mother liquor of the synthesis system added different amounts of NaCl (Fig.S4);

□5□(A) Si concentrations, (B) Al concentrations and (C) Si/Al ratios of the mother liquor of the synthesis system added different amounts of Na_2-EDTA (Fig.S5);

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□7□SEM images of samples synthesized with the synthesis gels added different amounts of Na_2-EDTA: (a) [Na_2-EDTA]/[SiO_2] = 0, pH was adjusted to 8.5 with concentrated sulfuric

acid, (b) [Na_2-EDTA]/[SiO_2] = 0.05, (c) [Na_2-EDTA]/[SiO_2] = 0.06, (d) [Na_2-EDTA]/[SiO_2] = 0.11, (e) [Na_2-EDTA]/[SiO_2] = 0.15 and (f) [Na_2-EDTA]/[SiO_2] = 0, without adjustment of pH value (9.3) with concentrated sulfuric acid (Fig.S7);

（8）TG curves of (A) deactivated HZSM-5-c1 and (B) H-ZSM-5-h(38) (Fig.S8);

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（13）Chemical compositions of the gels for synthesis of different samples (Table S1);

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（16）Acidic and textural properties of HZSM-5(38) and HZSM-5-c1 (Table S4);

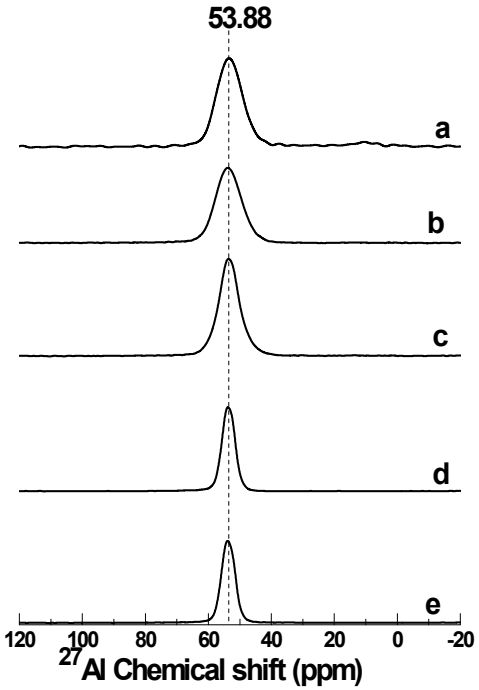

Fig.S1 ^{27}Al MAS NMR spectra of (a) ZSM-h(0), (b) ZSM-h(20), (c) ZSM-h(22), (d) ZSM-h(26), (e) ZSM-h(38).

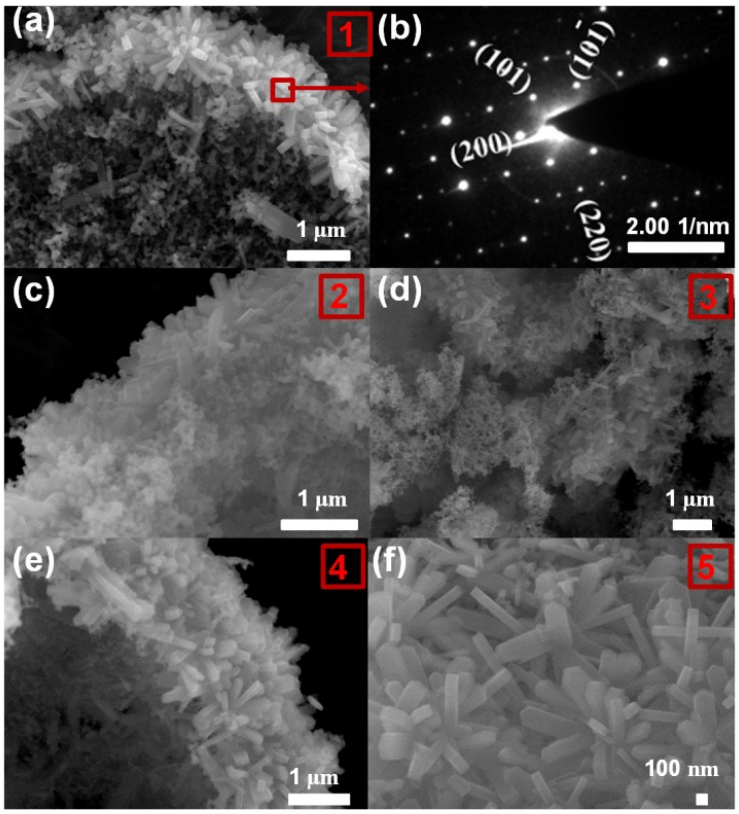

Fig.S2 Magnified SEM images (a, c, d, e, and f) of (a) ZSM-5-h(22), box 1 in Fig.4c, (c) shell of ZSM-5-h(24), box 2 in Fig. 4d, (d) core of ZSM-5-h(24), box 3 in Fig. 4d, (e) shell of ZSM-5-h(26), box 4 in Fig. 4e, (f) core of ZSM-5-h(26) , box 5 in Fig. 4e; and SEAD pattern of (b) ZSM-5-h(22), red box of shell.

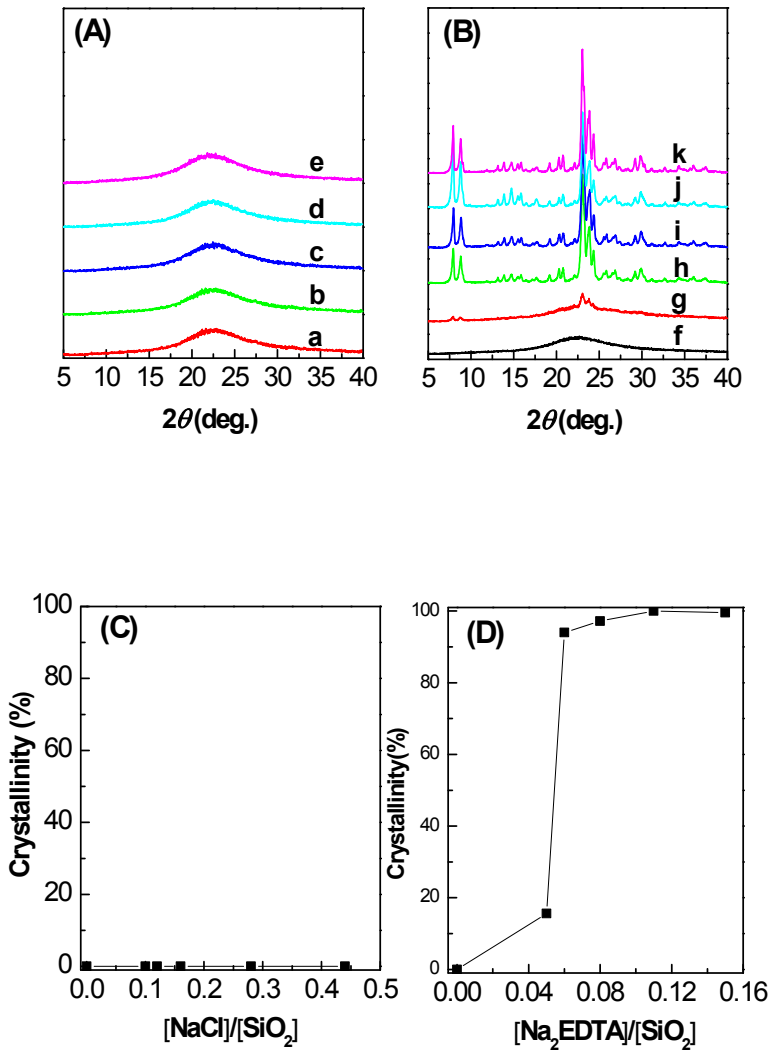

Fig.S3 (A) XRD patterns of the samples synthesized by adding different amounts of NaCl: (a) [NaCl]/[SiO_2] = 0.1, (b) [NaCl]/[SiO_2] = 0.12, (c) [NaCl]/[SiO_2] = 0.16, (d) [NaCl]/[SiO_2] = 0.28 and (e) [NaCl]/[SiO_2] = 0.44; (B) XRD patterns of the samples synthesized by adding different amounts of Na_2-EDTA: (f) [Na_2-EDTA]/[SiO_2] = 0, (g) [Na_2-EDTA]/[SiO_2] = 0.05, (h) [Na_2-EDTA]/[SiO_2] = 0.06, (i) [Na_2-EDTA]/[SiO_2] = 0.08, (j) [Na_2-EDTA]/[SiO_2] = 0.11, (k) [Na_2-EDTA]/[SiO_2] = 0.15; (C) the crystallinities of the samples synthesized by adding different amounts of NaCl; and (D) the crystallinities of the samples synthesized by adding different amounts of Na_2-EDTA.

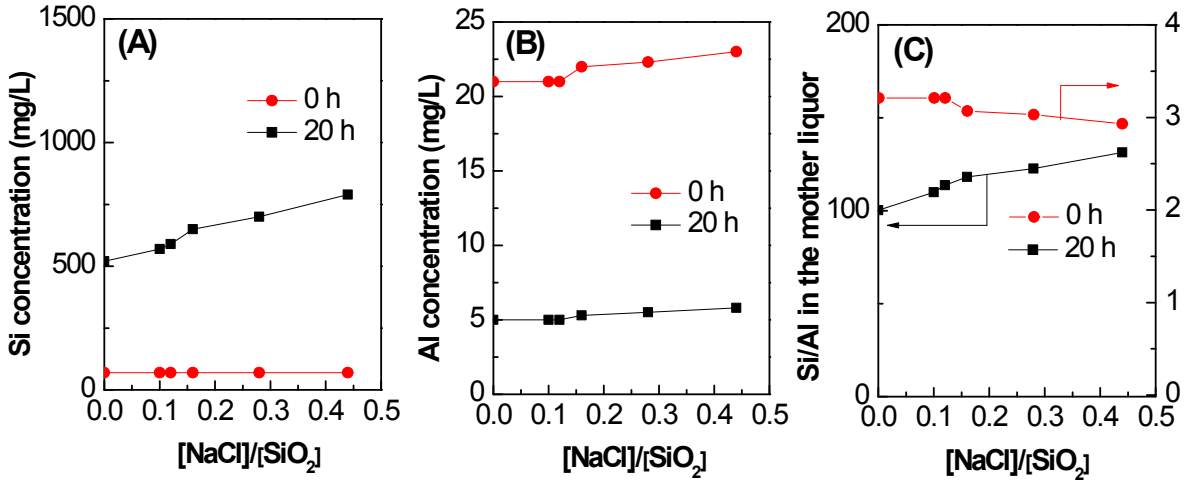

Fig.S4 (A) Si concentrations, (B) Al concentrations and (C) Si/Al ratios of the mother liquor of the synthesis system added different amounts of NaCl.

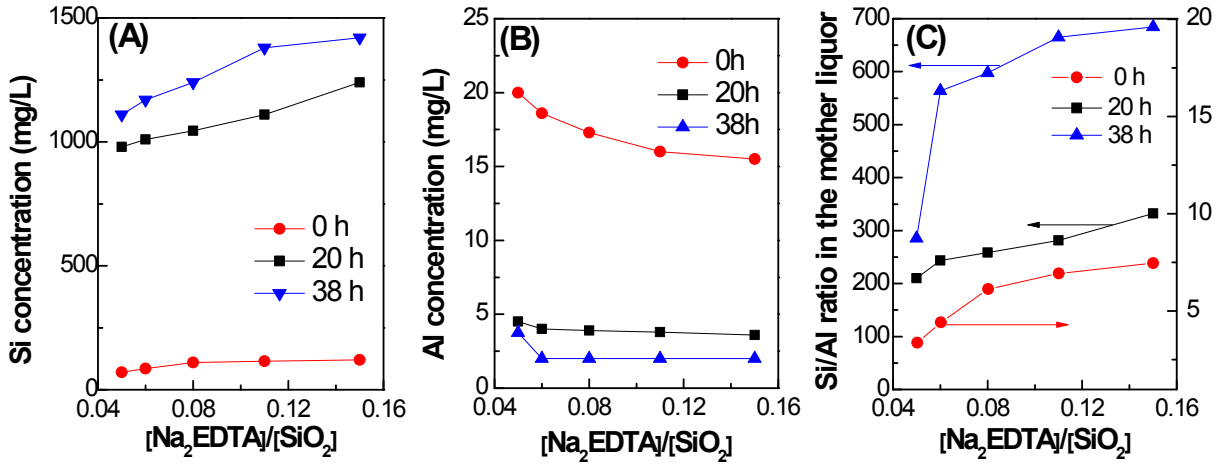

Fig.S5 (A) Si concentrations, (B) Al concentrations and (C) Si/Al ratios of the mother liquor of the synthesis system added different amounts of Na_2-EDTA.

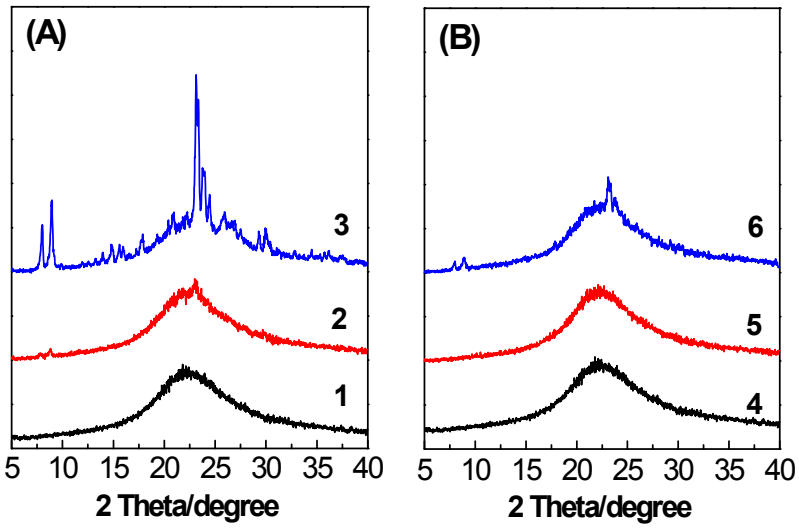

Fig.S6 XRD patterns of the samples synthesized at the pH value of (1, 4) 8.5, (2, 5) 10.5, (3, 6) 12.5 with the synthesis gels added (A) Na_2-EDTA but no butylamine template; (B) NaCl but on butylamine template.

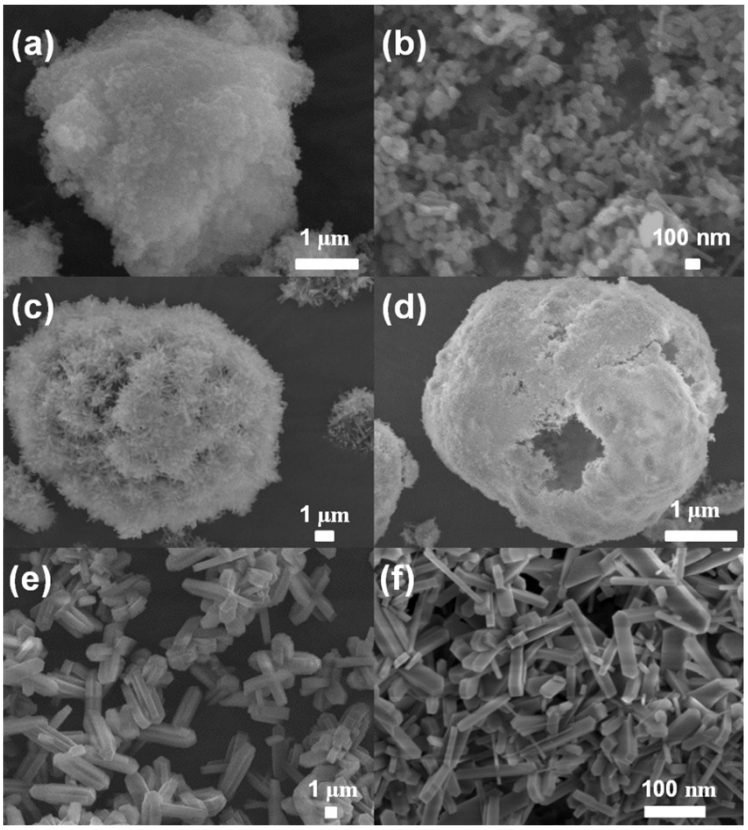

Fig.S7 SEM images of samples synthesized with the synthesis gels added different amounts of Na_2-EDTA: (a) [Na_2-EDTA]/[SiO_2] = 0, pH was adjusted to 8.5 with concentrated sulfuric acid, (b) [Na_2-EDTA]/[SiO_2] = 0.05, (c) [Na_2-EDTA]/[SiO_2] = 0.06, (d) [Na_2-EDTA]/[SiO_2] = 0.11, (e) [Na_2-EDTA]/[SiO_2] = 0.15 and (f) [Na_2-EDTA]/[SiO_2] = 0, without adjustment of pH value (9.3) with concentrated sulfuric acid.

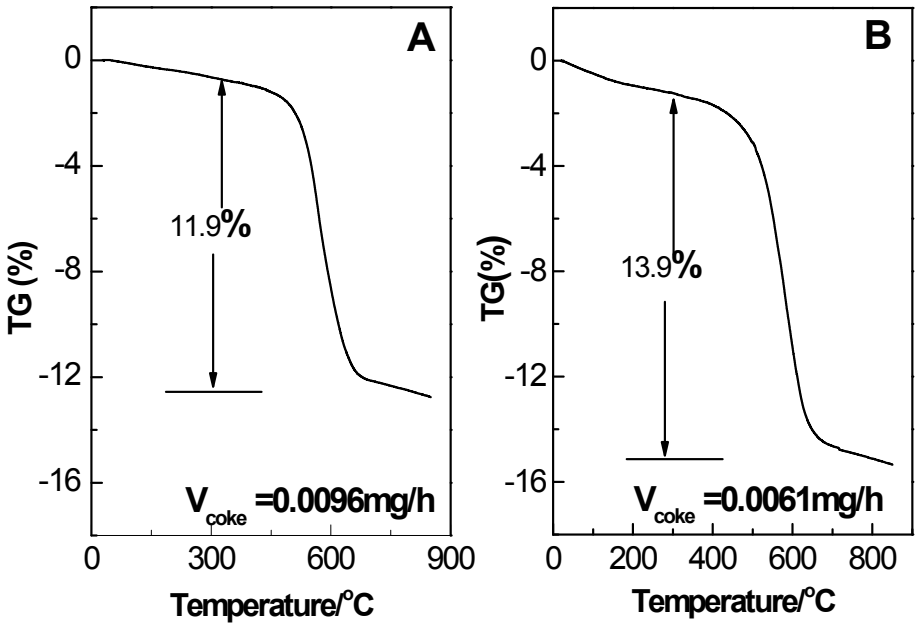

Fig.S8 TG curves of (A) deactivated HZSM-5-c1 and (B) H-ZSM-5-h(38).

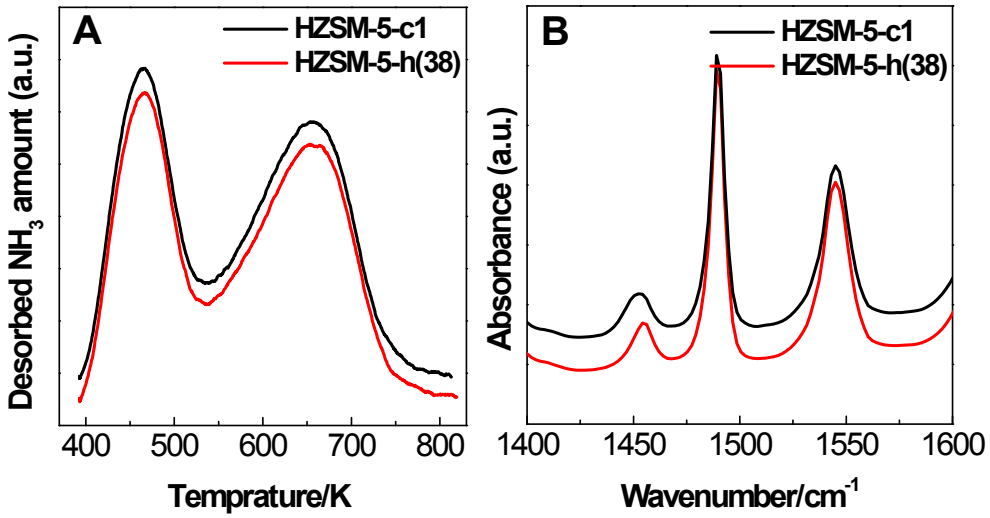

Fig.S9 (A) NH_3-TPD profiles and (B) Py-IR spectra of HZSM-5-h(38) and HZSM-5-c1.

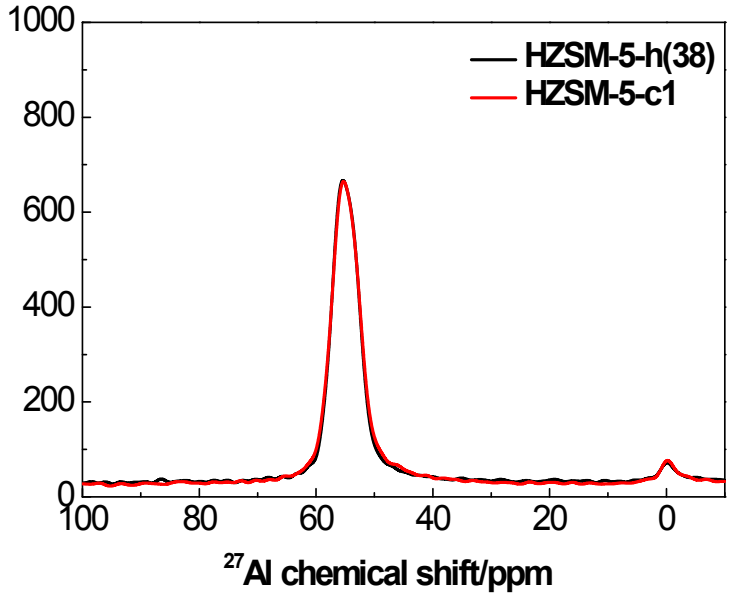

Fig.S10 ^{27}Al MAS NMR spectra of HZSM-5-h(38) and HZSM-5-c1.

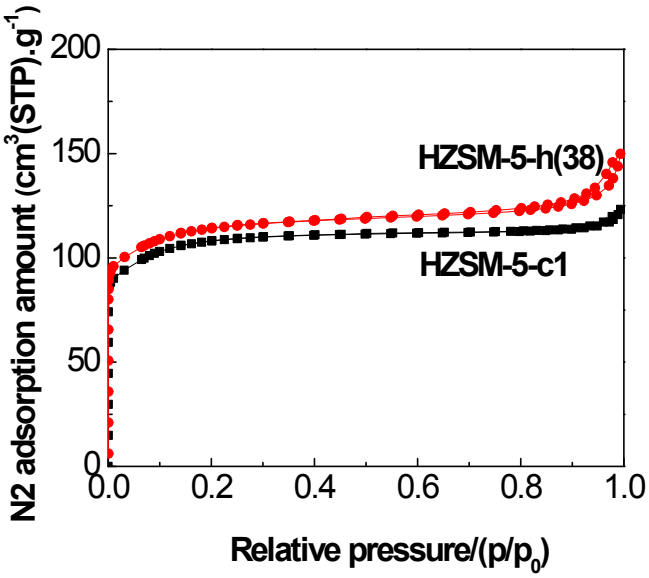

Fig.S11 Nitrogen adsorption-desorption isotherms of HZSM-5-h(38) and HZSM-5-c1.

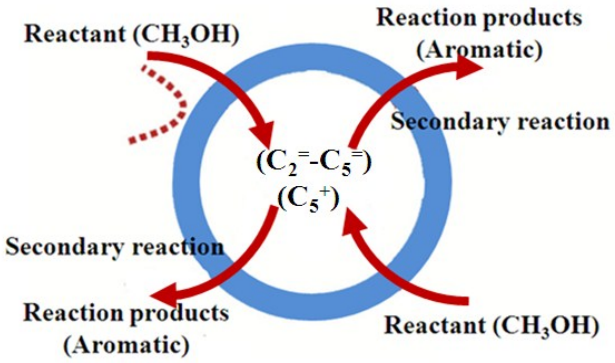

Fig.S12 Schematic illustration of the catalytic reaction process over ZSM-5 hollow spheres.

Table S1. Chemical compositions of the gels for synthesis of different samples.

Samples	Chemical compositions (molar ratio)	pH
ZSM-5-h	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.08Na_2EDTA	8.5
ZSM-5-a1	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.10NaCl	8.5 [a]
ZSM-5-a2	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.12NaCl	8.5 [a]
ZSM-5-a3	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.16NaCl	8.5 [a]
ZSM-5-a4	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.28NaCl	8.5 [a]
ZSM-5-a5	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.44NaCl	8.5 [a]
ZSM-5-b1	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA	8.5[a]
ZSM-5-b2	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.05Na_2EDTA	8.5[a]
ZSM-5-b3	SiO_2: 0.14 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.06 Na_2EDTA	8.5[a]
ZSM-5-b4	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.11 Na_2EDTA	8.5 [b]
ZSM-5-b5	SiO_2: 0.014 Al_2O_3: 0.09 Na_2O: 31H_2O: 0.15NBA: 0.15 Na_2EDTA	8.5 [b]
ZSM-5-c1	SiO_2: 0.014 Al_2O_3: 0.05 Na_2O: 31H_2O: 0.15NBA	9.3

[a] The pH value was adjusted with concentrated sulfuric acid;

[b] The pH value was adjusted with NaOH aqueous solution (5 mol/L).

Table S2. ^{29}Si MAS NMR data, framework and bulk Si/Al ratios of ZSM-5-h(n) samples.

Samples	Resonance (%)				Si/Al	
	Q^2	Q^3	Q^4	Si(3Si,1Al)	Framework[a]	Bulk[b]
ZSM-5-h(0)	1.4	4.1	84.5	10.5	--	35.7
ZSM-5-h(20)	3.7	10.9	72.4	13.0	--	31.9
ZSM-5-h(22)	1.8	2.7	82.6	12.8	--	31.0
ZSM-5-h(26)	0	2.0	85.3	12.7	31.5	31.4
ZSM-5-h(38)	0	1.0	86.2	12.8	31.3	31.5

[a] Determined by ^{29} Si MAS NMR data;

[b] Analyzed with ICP.

Table S3. Product distributions obtained over HZSM-5(38) and HZSM-5-c1 in methanol-to-aromatics process.

Samples	Production selectivity (%)				
	C_1^--C_4^-	$C_2^=$-$C_5^=$	C_5^+	Aromatics	Others
HZSM-5-h(38)	37.7	4.9	16.1	40.1	1.3
HZSM-5-c1	35.4	6.3	23.2	33.9	1.2

Reaction conditions: 390 ^oC, 0.5 MPa, $WHSV_{methanol}$ of 3.2 h^{-1}.

The data were acquired at the time on stream (TOS) of 12 h, and the methanol conversions in both cases are higher than 99.5%.

Table S4. Acidic and textural properties of HZSM-5(38) and HZSM-5-c1.

Samples	Acid sites ($mol \cdot g^{-1}$)					S_{BET} ($m^2 \cdot g^{-1}$)	V_{micro} ($cm^3 \cdot g^{-1}$)	V_{meso} ($cm^3 \cdot g^{-1}$)
	Strong	Weak	Total	Brønsted	Lewis			
HZSM-5-h(38)	0.453	0.292	0.745	0.304	0.048	349	0.10	0.16
HZSM-5-c1	0.444	0.296	0.740	0.315	0.059	341	0.10	0.10