Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Space-confined Synthesis of Nanorods Oriented-assembled Hierarchical MFI Zeolite Microspheres

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Scetion I: Synthesis of Materials

(1) Synthesis of carbon/silica monolith (SiO_2/C = 4:6)

In this case, the reaction mixture having the batch molar composition 0.64glucose-0.92resorcinol-20H_2O-0.25TsOH-TEOS was prepared by mixing glucose, resorcinol, and TsOH in deionized water to form a transparent solution in a Teflon-line container, followed by addition of TEOS under stirring at 80 ºC. Afterwards, this container was sealed into an autoclave and put into an oven of 180 ºC for 24 h for hydrothermal treatment. The resultant monolith was washed with hot distilled water (>80 ºC) until no sulfate ions were detected in the filtration water, and then dried at 90 ºC overnight. After that, the composite monolith was further carbonized at 500 ºC in N_2 atmosphere at a heating rate of 2 ºC min^{-1}.

(2) Catalytic reactions

All ZSM-5 samples were transferred to H^+ type ZSM-5 by ion exchange with NH_4NO_3 (1 mol L^{-1}) at 80 ºC for 3 h, which repeated three times, finally all the catalysts were calcined at 550 ºC for 3 h.

Condensation of benzaldehyde with n-butyl alcohol

The catalytic reactions were carried out under N_2 in a three-necked flask equipped with a refluxing condenser. In a typical run, 1.325 g of benzaldehyde, 3.7 g of n-butyl alcohol and 0.05 g of Hier-ZSM-5 were mixed with continuous stirring, then the reaction temperature was raised to and kept at 80 ºC for 4 h. The reaction mixtures were separated by centrifugation and analyzed by a Perkin-Elmer Clarus 500 gas chromatography with a SE-54 column. The product was further confirmed by GC-MS.

Alkylation of toluene with benzyl chloride

The catalytic reactions were carried out under N_2 in a three-necked flask equipped with a reflux condenser. In a typical run, 1.38 g of toluene, 1.9 g of benzyl chloride and 0.05 g of Hier-ZSM-5 were mixed with stirring, then the reaction temperature was raised and kept at 80 ºC for 3 h. The reaction mixtures were separated by centrifugation and analyzed by a Perkin-Elmer Clarus 500 gas chromatography with a SE-54 column. The products were further confirmed by GC-MS.

Acetalization of cyclohexanone

The acetalization of cyclohexanone was carried out batch-wise in around-bottomed flask equipped with a condenser and a magnetic stirrer. In a typical reaction, 0.05 g of Hier-ZSM-5 was dispersed in a solution containing 10 mL of methanol and 0.098 g of cyclohexanone. The solution was stirred at 50 ºC for 4 h and then the reaction mixtures were separated by centrifugation and analyzed by a Perkin-Elmer Clarus500 gas chromatography with a SE-54 column. The product was

further confirmed by GC-MS.

Hydroxylation of Phenol with H_2O_2

Phenol hydroxylation experiments were carried out batch-wise in a round-bottomed flask equipped with a condenser and a magnetic stirrer. In a typical run, 1.28 g of phenol, 0.05 g of Hier-TS-1, and 10 mL of water were mixed, followed by an addition of H_2O_2 (30%, 0.51 g). After the reaction for 4 h at 80 ºC with magnetic stirring, the products were taken out from the system and analyzed by an HPLC apparatus (Agilent 1200 Series) equipped with an XDB-C18 column (Eclipse USA).

Section II: Supplemental Figures and Tables

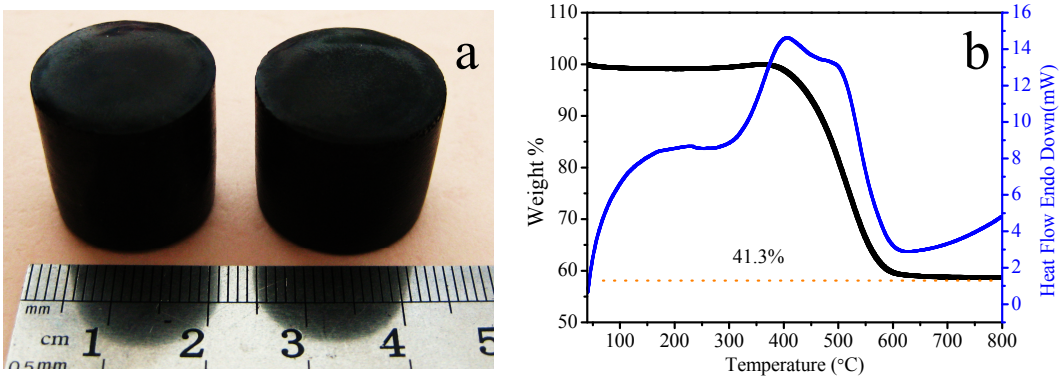

Figure S1 Photograph (a) and TG-DTA curves (b) of carbon/silica monolith (SiO_2/C = 6:4).

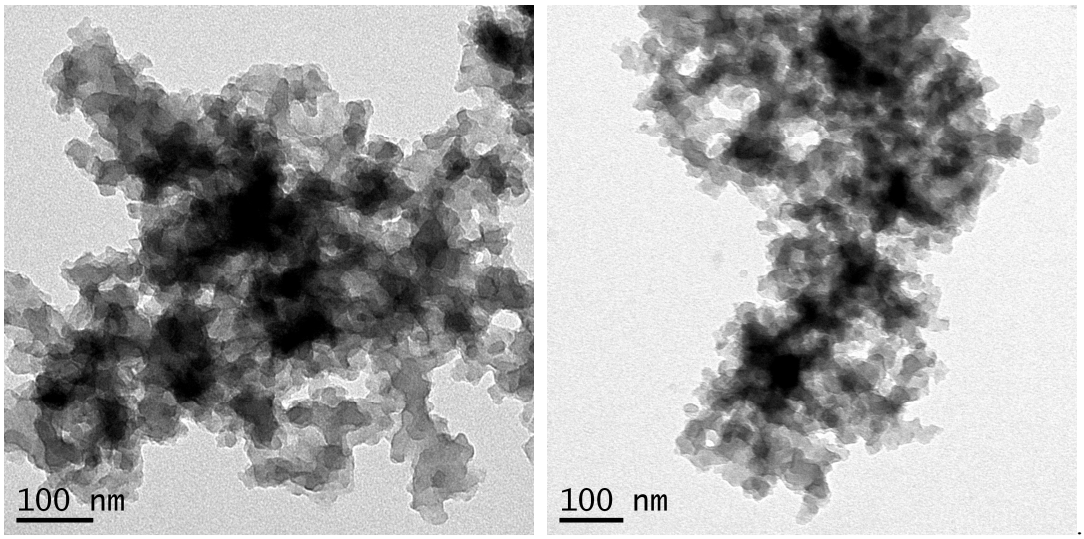

Figure S2 TEM images of carbon after etching silica with HF acid.

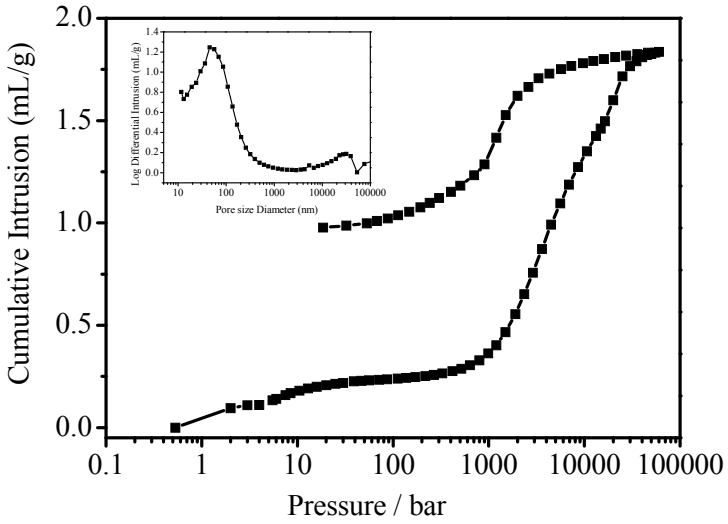

Figure S3 Mercury intrusion porosimetry investigations of carbon after etching silica with HF acid.

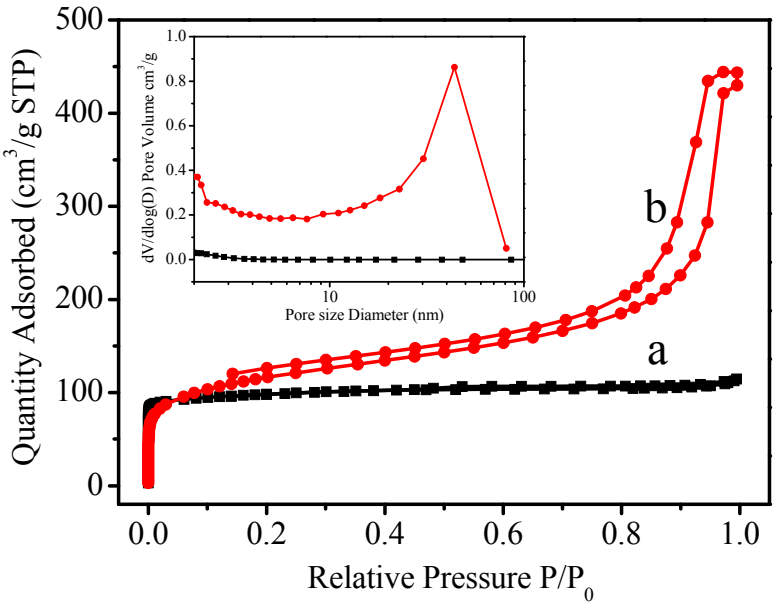

Figure S4 N_2 sorption isotherms and pore size distributions (inset) of (a) carbon/silica monolith (SiO_2/C = 6:4) and (b) carbon after etching silica with HF acid.

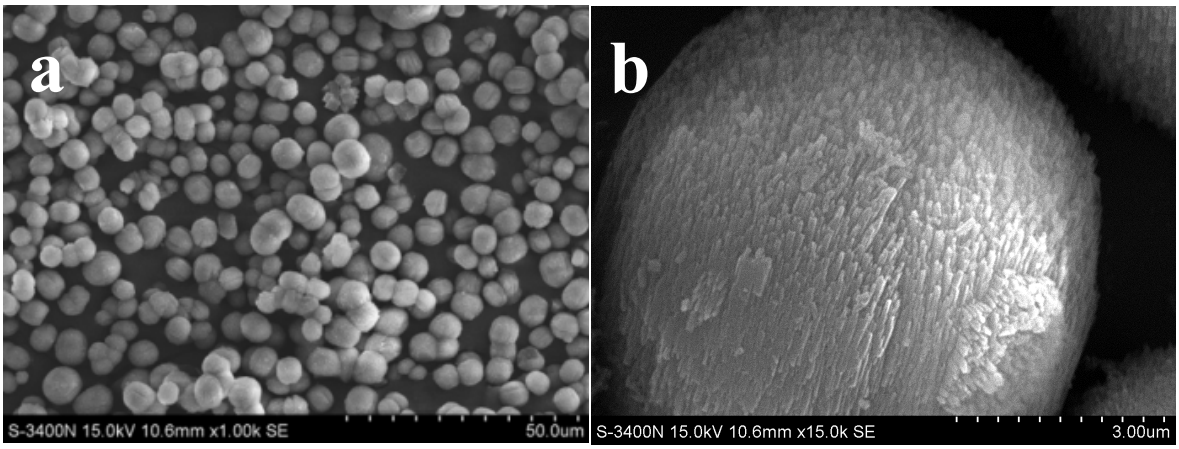

Figure S5 SEM images of (a) Hier-Silicalite-1 and (b) Hier-Silicalite-1 after 1 h of ultrasonic treatment.

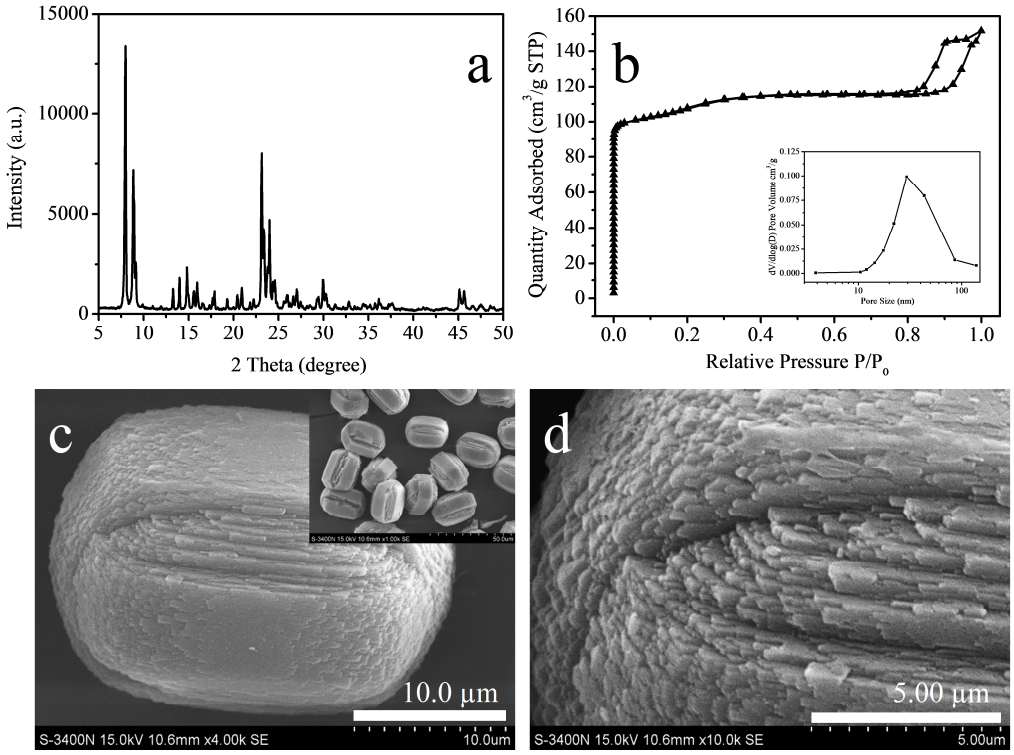

Figure S6 XRD patterns (a), N_2 sorption isotherms (b) and SEM images (c and d) of Silicalite-1 synthesized from carbon/silica monolith (SiO_2/C = 6:4) without N_2 treatment (designated as Hier-Silicalite-1 (WONT)).

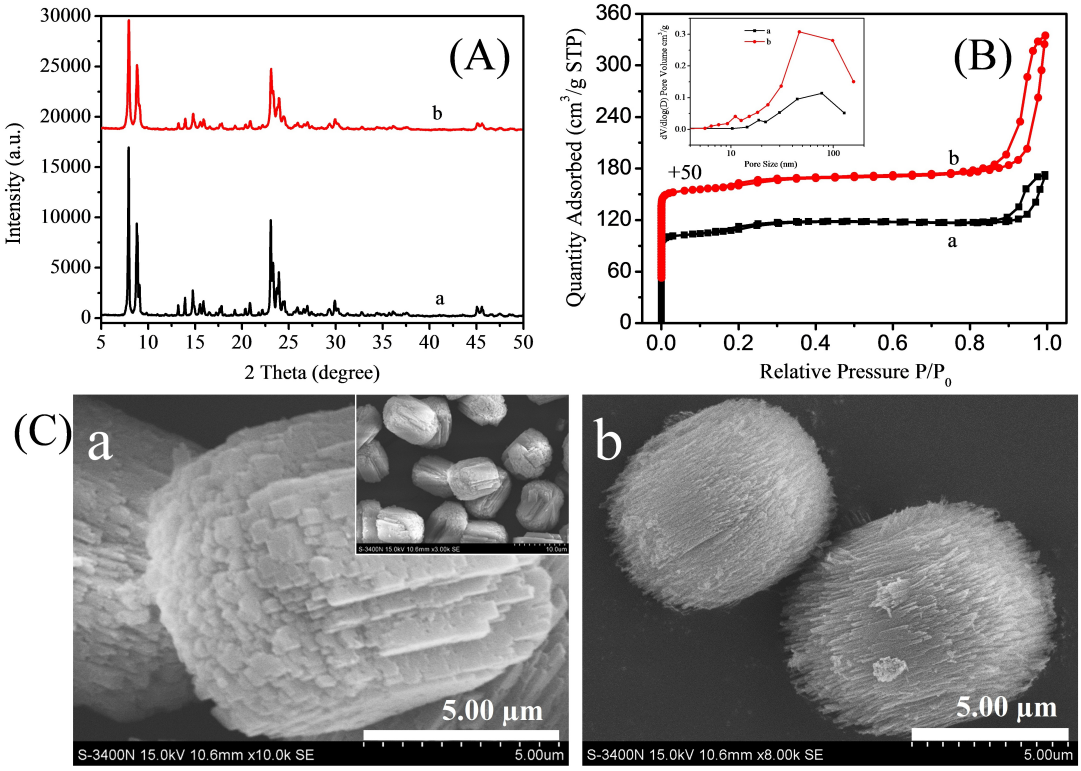

Figure S7 XRD patterns (A), N_2 sorption isotherms (B) and SEM images (C) of Silicalite-1 synthesized from carbon/silica composite monolith (SiO_2/C = 4:6) without N_2 treatment (a, designated as meso-Silicalite-1 (4:6-WONT)) and with N_2 treatment (b, designated as Hier-Silicalite-1 (4:6)).

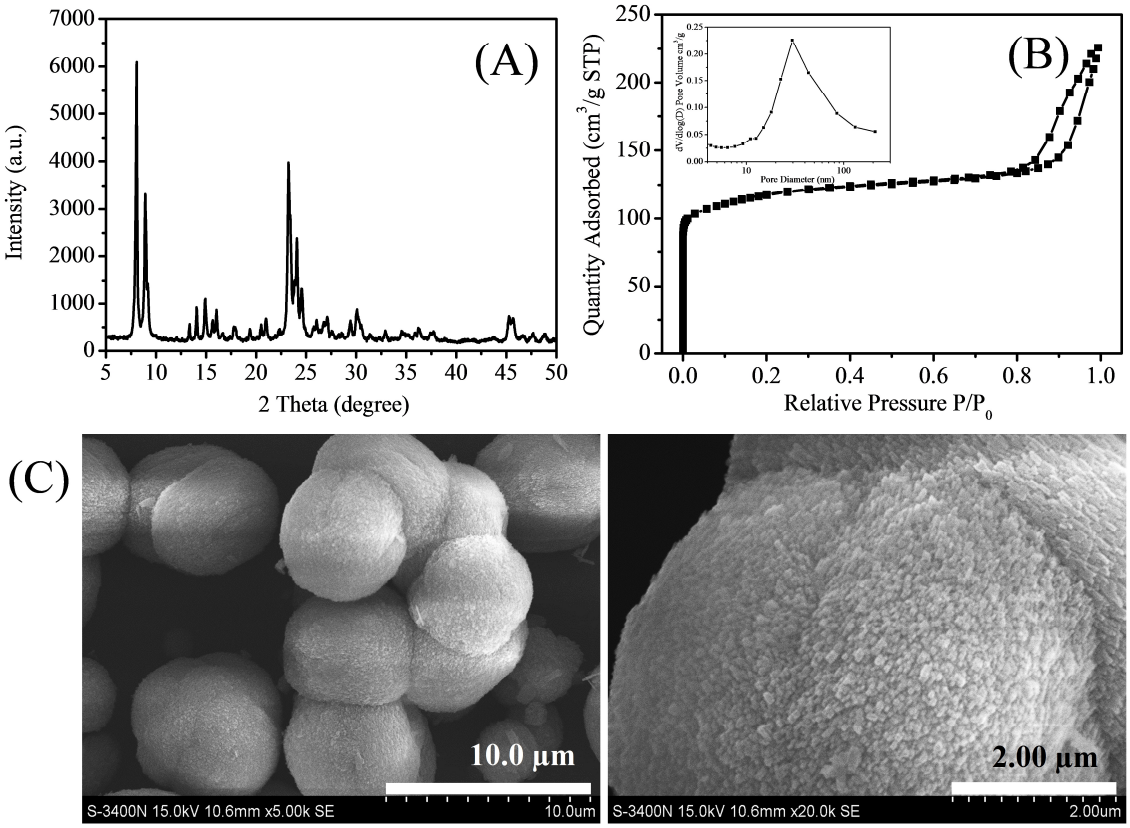

Figure S8 XRD patterns (A), N_2 sorption isotherms (B) and SEM images (C) of Silicalite-1 from carbon/silica composite (SiO_2/C = 7:3, not monolith) with N_2 treatment (designated as Hier-Silicalite-1 (7:3)).

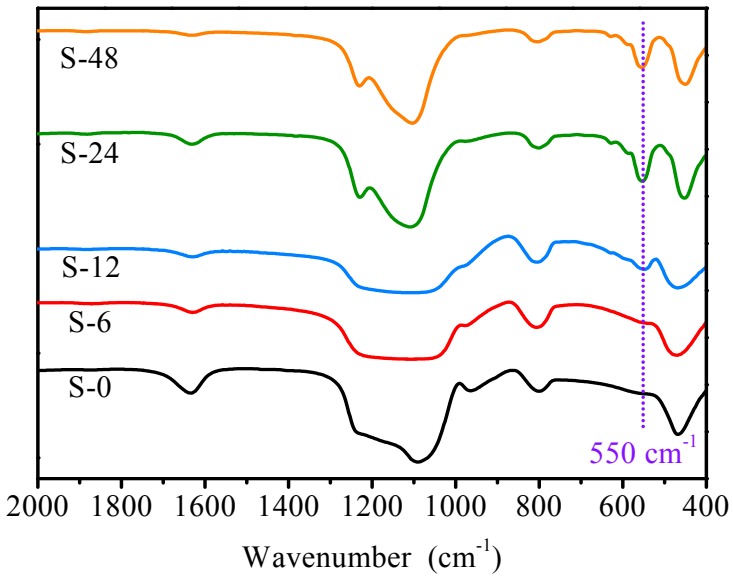

Figure S9 FT-IR spectra of the samples at various reaction times.

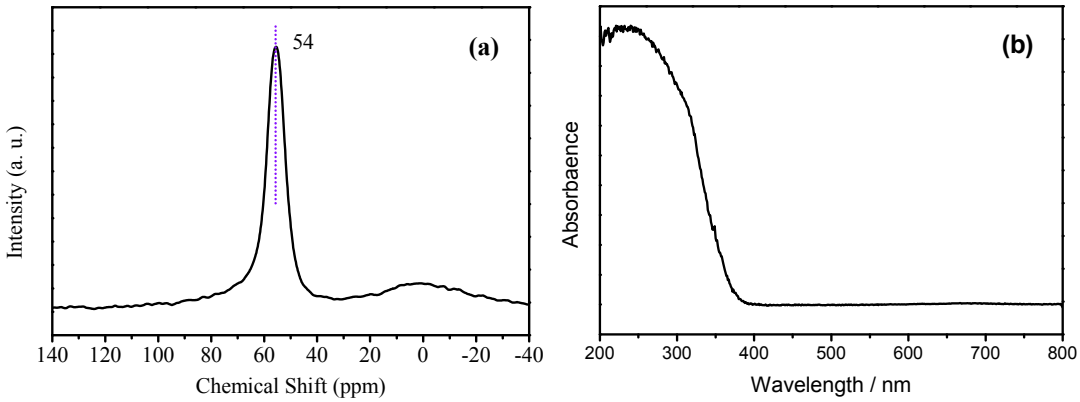

Figure S10 (a) ^{27}Al solid state NMR spectra of Hier-ZSM-5 and (b) UV-vis spectra of Hier-TS-1.

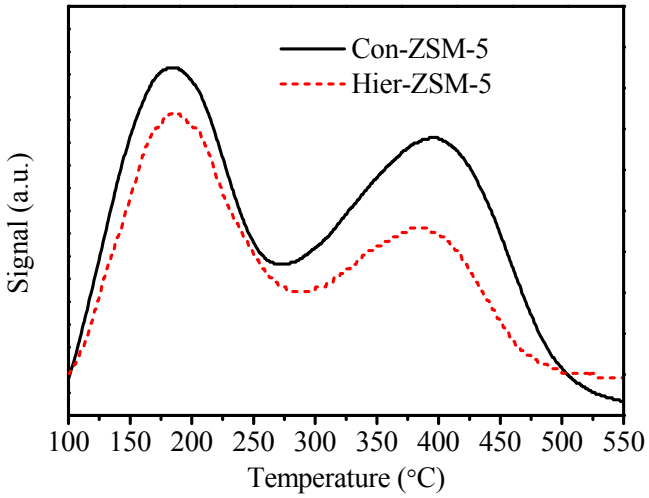

Figure S11 NH_3-TPD curves of Con-ZSM-5 and Hier-ZSM-5.

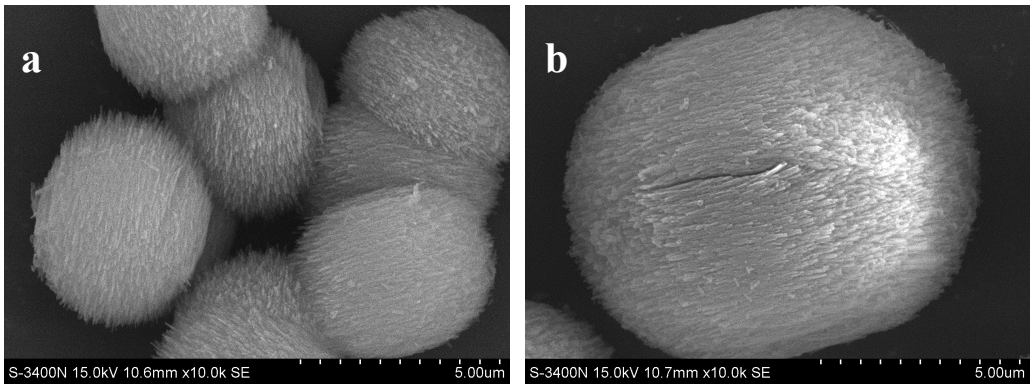

Figure S12 SEM images of Hier-ZSM-5 after 1 h of ultrasonic treatment (a) and after condensation reaction (b).

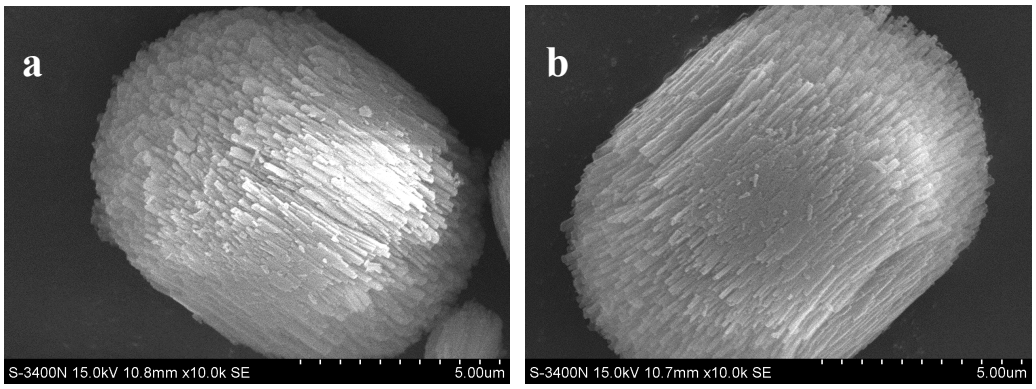

Figure S13 SEM images of Hier-TS-1 after 1 h of ultrasonic treatment (a) and after phenol hydroxylation reaction (b).

Table S1 Textural parameters of carbon after etching silica by HF acid.

Samples	S_{BET} ($m^2\ g^{-1}$)	S_{micro} ($m^2\ g^{-1}$)[a]	V_{mirco} ($cm^3\ g^{-1}$)[a]	V_{total} ($cm^3\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)[b]
carbon/silica monolith	354	278	0.15	0.17	-
carbon	418	148	0.06	0.66	1.84

a: determined by the t-plot method, b: obtained by mercury porosimetry.

Table S2 Textural parameters of samples synthesized under different conditions

Samples	Crystallization time (h)	S_{BET} ($m^2\ g^{-1}$)	S_{micro} ($m^2\ g^{-1}$)[a]	V_{mirco} ($cm^3\ g^{-1}$)[a]	V_{meso} ($cm^3\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)
Hier-Silicalite-1 (WONT)	96	383	268	0.12	0.11	0.23
Hier-Silicalite-1 (4:6)	96	394	277	0.12	0.30	0.42
Hier-Silicalite-1 (4:6-WONT)	96	388	249	0.11	0.15	0.26
Hier-Silicalite-1 (7:3)	96	401	265	0.12	0.22	0.34

a: determined by the t-plot method

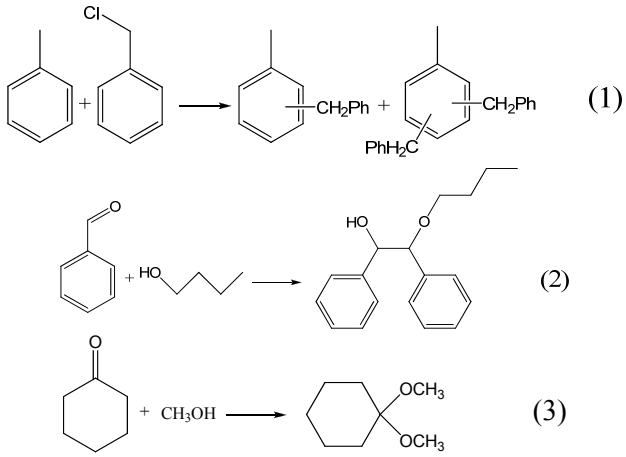

Table S3 Catalytic performance of Hier-ZSM-5 and Con-ZSM-5

Reaction		Hier-ZSM-5	Con-ZSM-5
1	**Toluene conversion (%)**	**73.5 (90:10)[a]**	**30.0 (99:1)**
2	**Benzaldehyde conversion (%)**	**54.1**	**19.5**
3	**Cyclohexanone conversion (%)**	**90.4**	**84.1**

(a) The first data value represents the reactant conversion (%). The numbers in parentheses indicates the percentage selectivity of mono-alkylated/di-alkylated product.

Table S4 Catalytic performance of Hier-TS-1 and TS-1 in phenol hydroxylation

Catalyst	Phenol conversion(%)	Product selectivity(%)		
		A	B	C
Hier-TS-1	**29.8**	**36.5**	**40.1**	**23.4**
TS-1	**15.7**	**34.3**	**38.6**	**27.1**

Product: A.catechol; B. hydroquinone; C. byproducts including Benzoquinone, tar and some unidentified products.