Electronic Supplementary Information

Engineering Growth Defects: A New Route Towards Hierarchical ZSM-5 Zeolite with High-density Intracrystalline Mesopores

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Experimental section

Synthesis of mesoporous ZSM-5 (M-ZSM-5-PDDA)

M-ZSM-5-PDDA was prepared using cationic polymer PDDA as the mesostructured soft template and TPAOH as the OSDA according to our previous report.[1] In a typical synthesis, 6.5 mL of TPAOH (25%) were added into a mixture of 6.9 mL of water and 0.27 mL of 1M NaOH aqueous solution, and then 1.5 g PDDA was added into the obtained solution under stirring. After PDDA completely dissolved in the solution, 4.5 mL of TEOS were added into the solution dropwise under stirring, followed by the addition of 0.042 g of isopropyl aluminates. After stirring for 24-48 h, the obtained sol was transferred into an autoclave for further crystallization at 180 ℃ for 2 days. The product was collected by filtration, dried in air and calcined at 550 ℃ to remove the templates.

Synthesis of ZSM-5 large crystals (LC-ZSM-5)

In a typical synthesis, 100 mg of aluminium isopropoxide, 1.33 g of TPABr and 0.2 g of NaOH were dissolved in 18 mL of water. After that, 11.5 mL of TEOS was rapidly added and stirred 12 h at room temperature. Then the mixture was transferred to a stainless steel autoclave with a Teflon container and hydrothermally treated at 180 ℃ for 48 h. The products were collected by filtration, washed with copious amount of water and dried at 80 ℃ overnight. The organic template was removed by calcination at 550 ℃ in air for 6 h.

Supplementary Figures and Legends

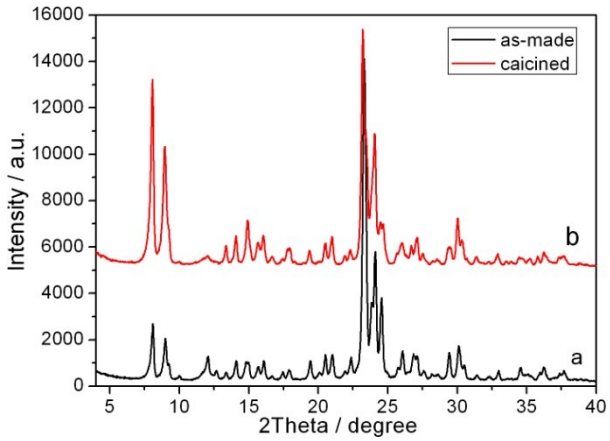

Figure S1. PXRD patterns of as-made (a) and calcined (b) HCN-ZSM-5-100/10d.

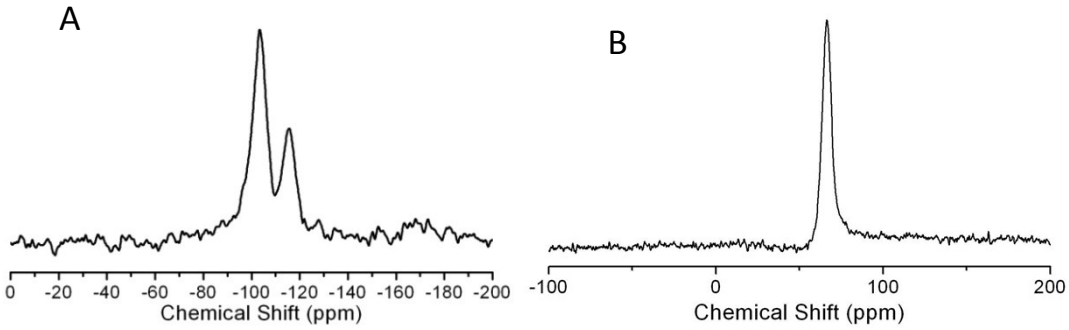

Figure S2. Solid-state ^{29}Si NMR spectrum (A) and ^{27}Al NMR spectrum (B) of calcined HCN-ZSM-5-100/10d.

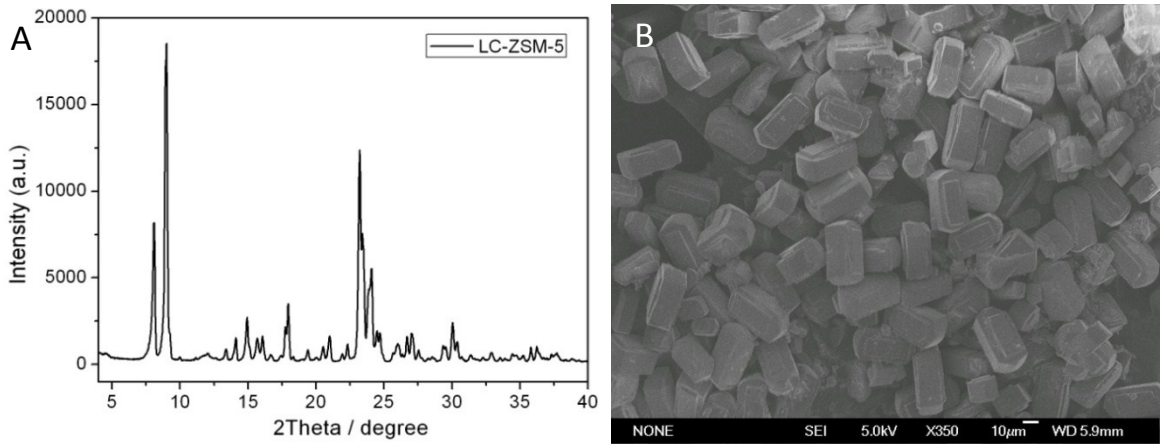

Figure S3. XRD pattern (A) and SEM image (B) of ZSM-5 large crystal (LC-ZSM-5) prepared using TPABr as the OSDA.

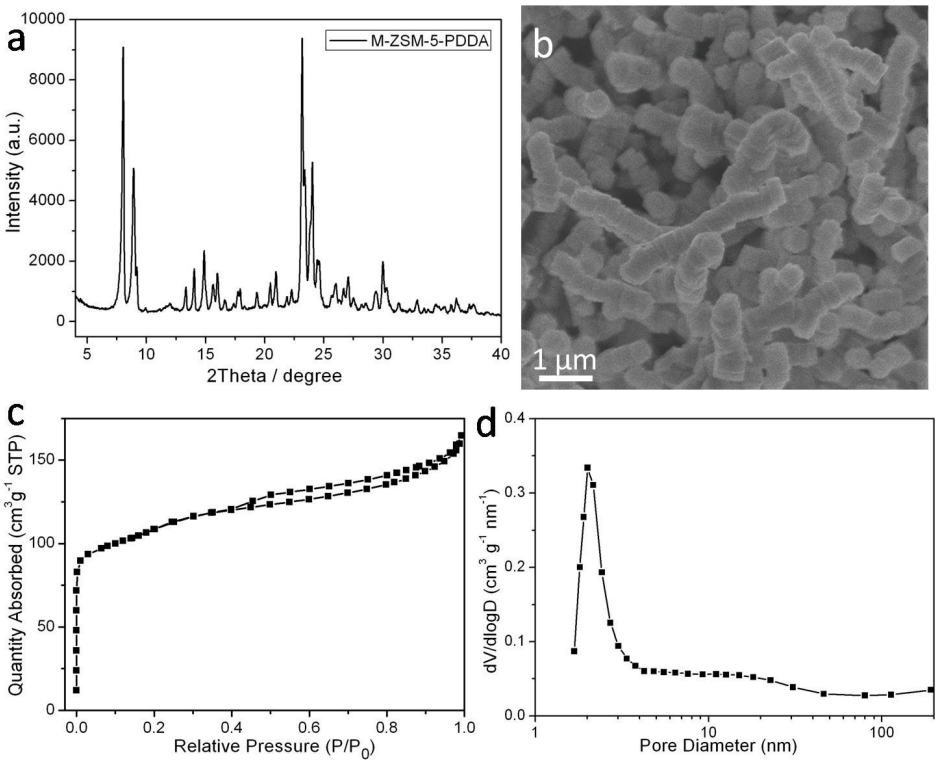

Figure S4. XRD pattern (a), SEM image (b), N_2 sorption isotherm (c) and pore size distribution curve (d) of mesoporous ZSM-5 (M-ZSM-5-PDDA) with self-stacked morphology prepared using cationic polymer PDDA as the mesostructured soft template and TPAOH as the OSDA.

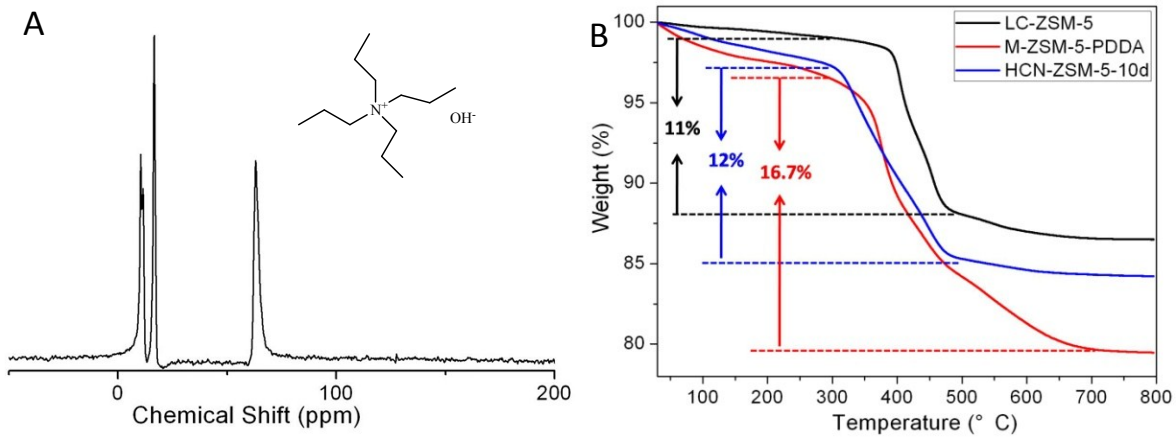

Figure S5. (A) Solid state ^{13}C NMR spectrum of as-made HCN-ZSM-5-100/10d; (B) TG curves of different as-made ZSM-5 samples: LC-ZSM-5 (black), M-ZSM-5-PDDA (red), HCN-ZSM-5-100/10d (blue).

Three sharp peaks in ^{13}C NMR spectrum can be clearly assigned to the TPA^+, indicating that TPA^+ is the only organic molecule in as-made HCN-ZSM-5-100/10d sample. Moreover, thermogravimetric analysis showed a similar weight loss (12%) with the conventional LC-ZSM-5 (11%) in the range of 300-500 ℃, corresponding to decomposition of TPA^+. These data indicate that the formation of uniform intracrystalline mesopores (2.2 nm) cannot be ascribed to the

contribution of TPA^+-based clusters and oligomers.

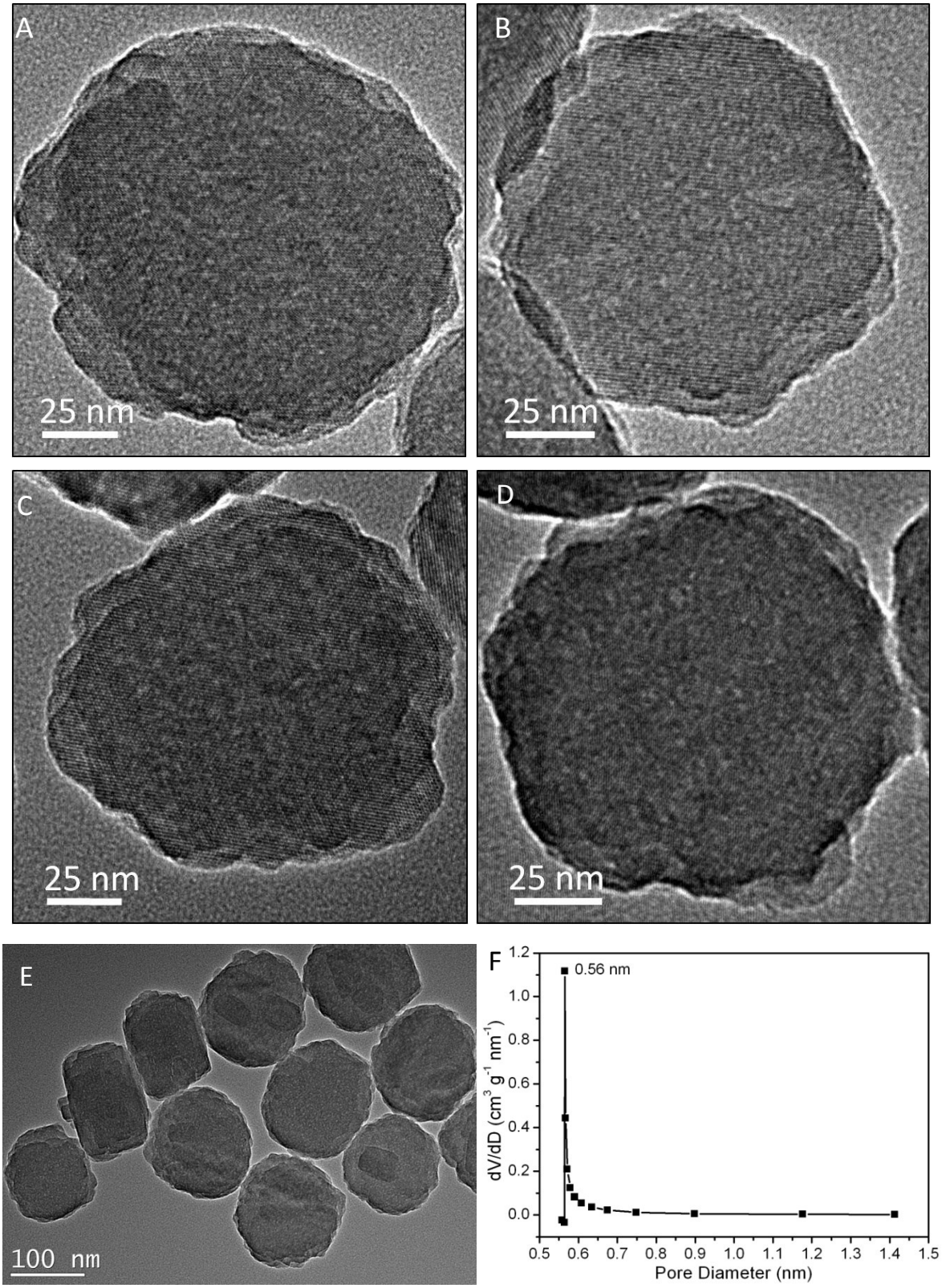

Figure S6. (A, B, C, D) TEM images of HCN-ZSM-5-100/10d individual nanocrystal with different crystal lattice plane. (E) Low-magnification TEM image of HCN-ZSM-5-100/10d. (F) Horvath-Kawazoe (HK) pore size distribution curve of calcined HCN-ZSM-5-100/10d.

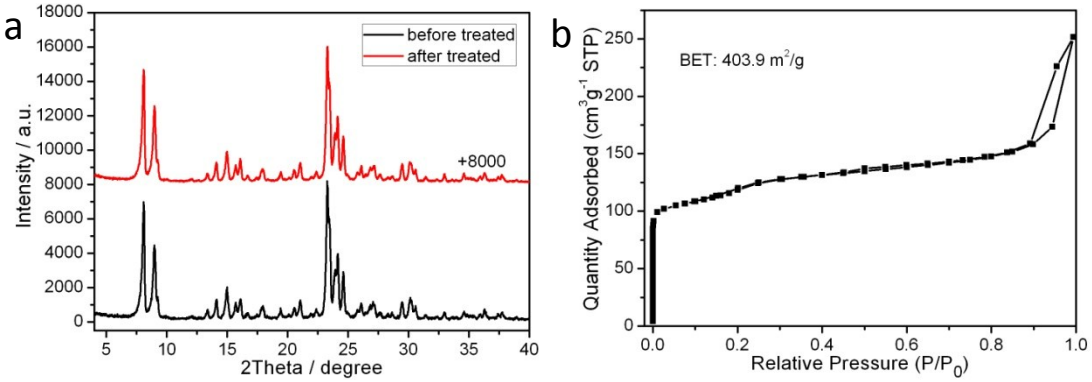

Figure S7. XRD pattern (a) and N_2 sorption isotherm (b) of the sample treated in boilling water for 48 h.

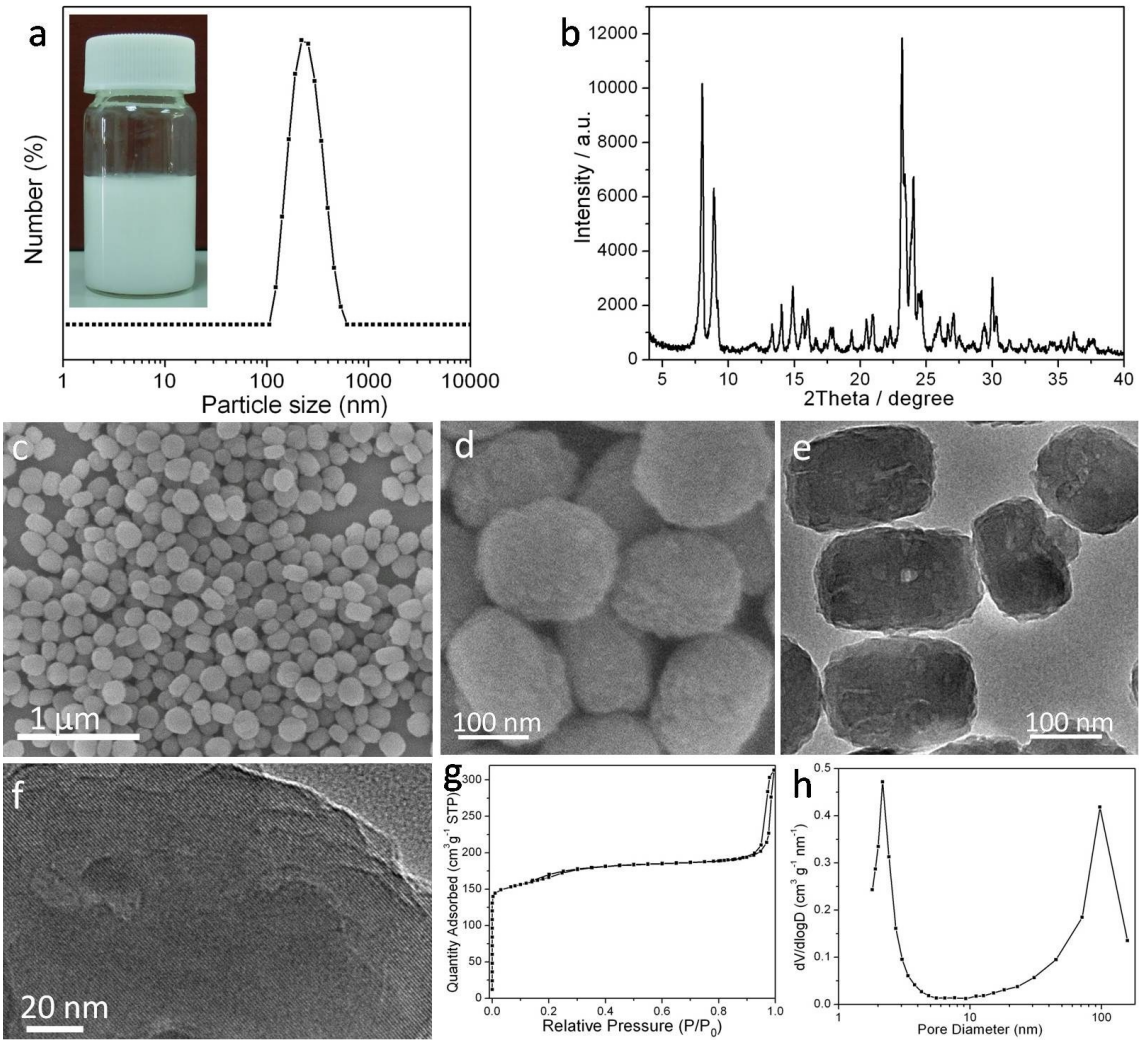

Figure S8. DLS (a), XRD pattern (b), SEM images (c, d), TEM image (e, f), N_2 sorption isotherm (g) and pore size distribution curve (h) of the HCN-ZSM-5-100/3d sample prepared under the same conditions for HCN-ZSM-5-100/10d except using half of the initial concentration of TPAOH (TPA/Si=5.5/25) and shorter crystallization time (3 days); the inset in a is relevant photograph of as-obtained HCN-ZSM-5 milk-like colloid aqueous.

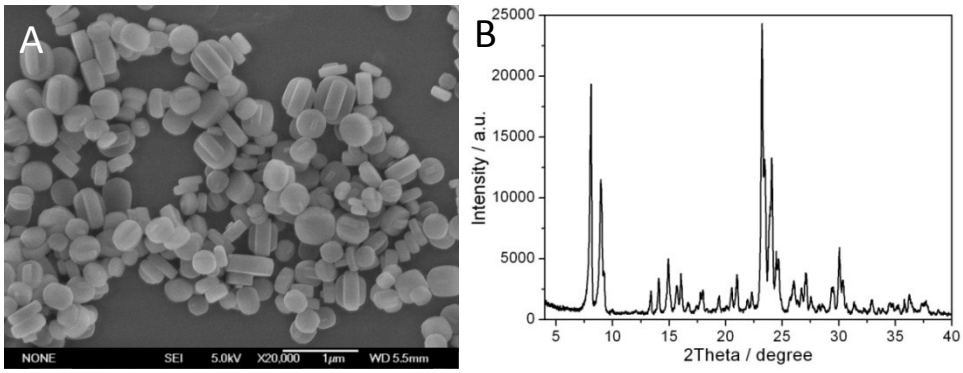

Figure S9. SEM image (A) and PXRD pattern (B) of the micrometer-sized ZSM-5 twin crystals prepared under the same conditions for HCN-ZSM-5-100/10d except using 4 mL of TPAOH (TPA/Si=3.7/25) and shorter crystallization time (3 days).

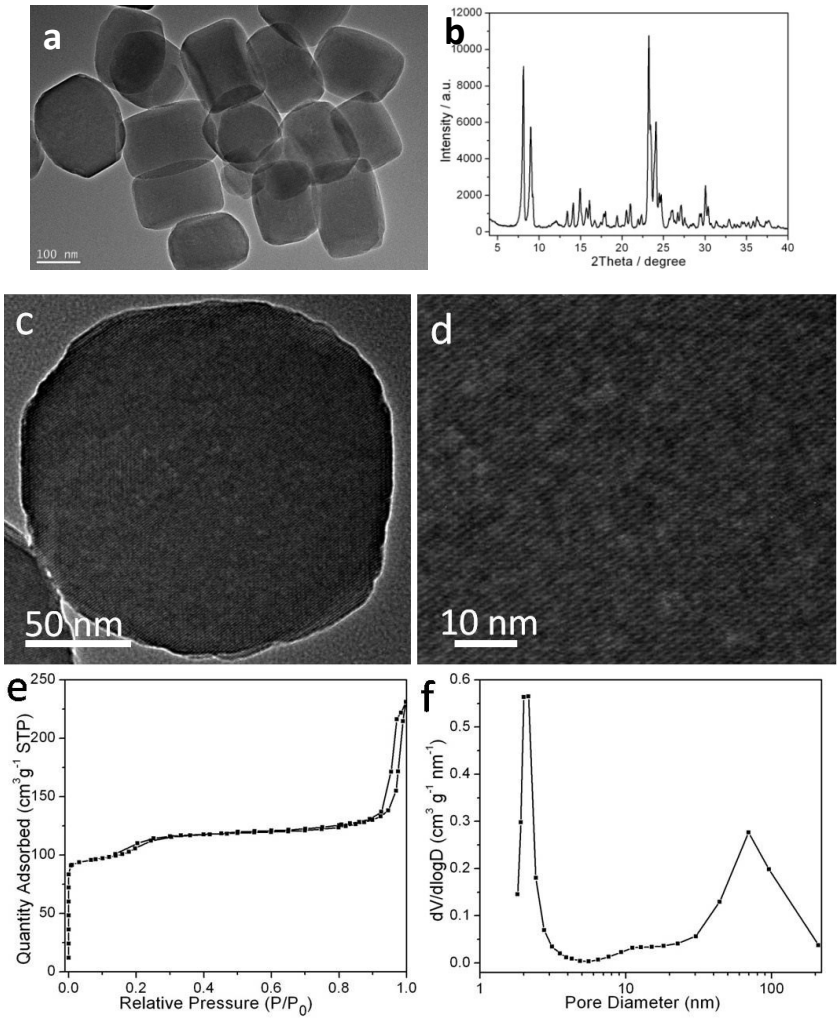

Figure S10. Low-magnification TEM image (a) and XRD pattern (b), high-magnification TEM images (c, d), N_2 sorption isotherm (e) and pore size distribution curve (f) of the sample HCN-ZSM-5-160/12h prepared under the same conditions for HCN-ZSM-5-100/10d except using

higher crystallization temperature (160 ℃) and shorter crystallization time (12 h).

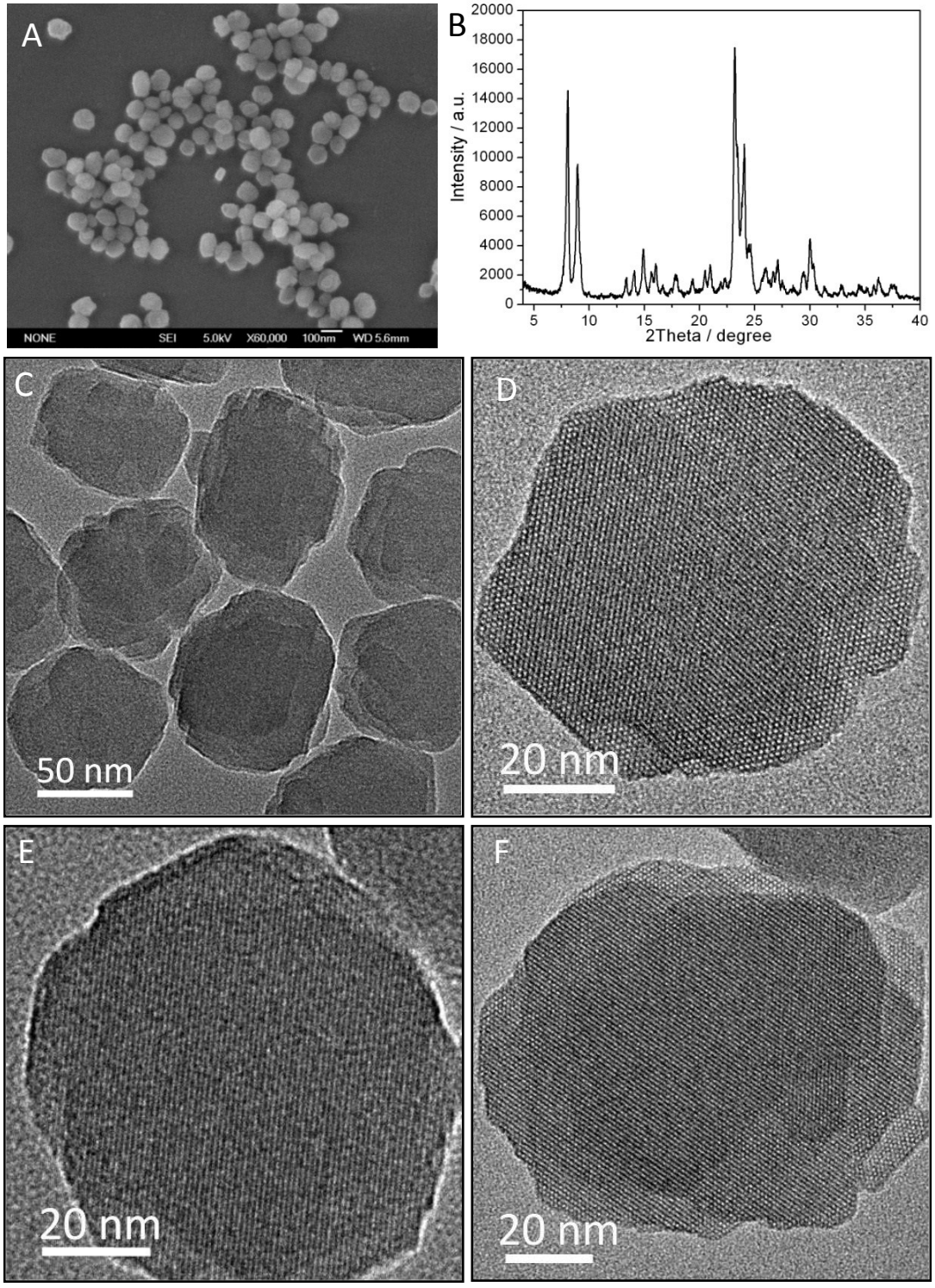

Figure S11. SEM image (A), XRD pattern (B) and TEM image (C) of Silicate-1 nanocrystals prepared under the same condition for HCN-ZSM-5-100/3d except the absence of aluminium isopropoxide; (D, E, F) TEM images of the relevant individual nanocrystal with different crystal lattice plane. These images further confirm that there are no intracrystalline mesopores or growth defects inside Silicate-1 nanocrystals.

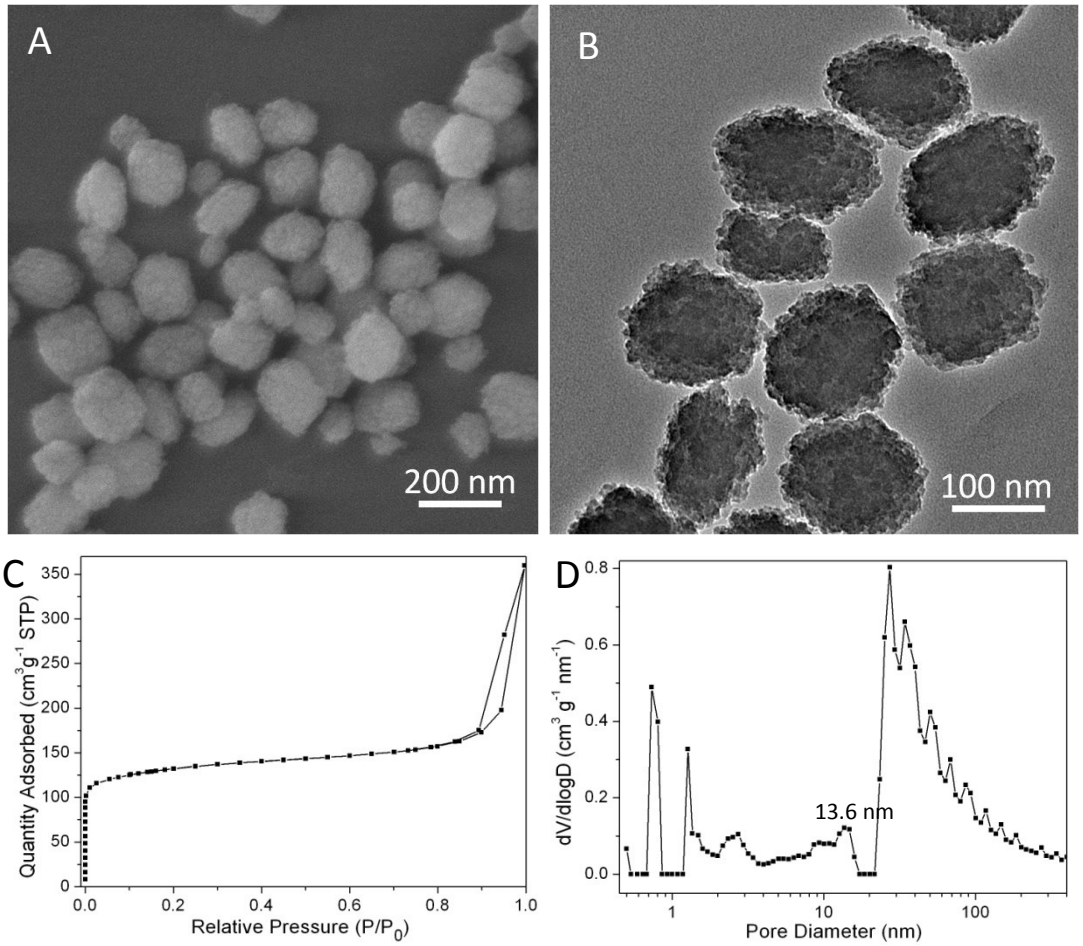

Figure S12. SEM image (A), TEM image (B), N_2 sorption isotherm (C) and pore size distribution curve (D) of calcined Nano-ZSM-5-60 sample prepared under the same condition for HCN-ZSM-5-100/3d except for using an original Si/Al ratio of 60.

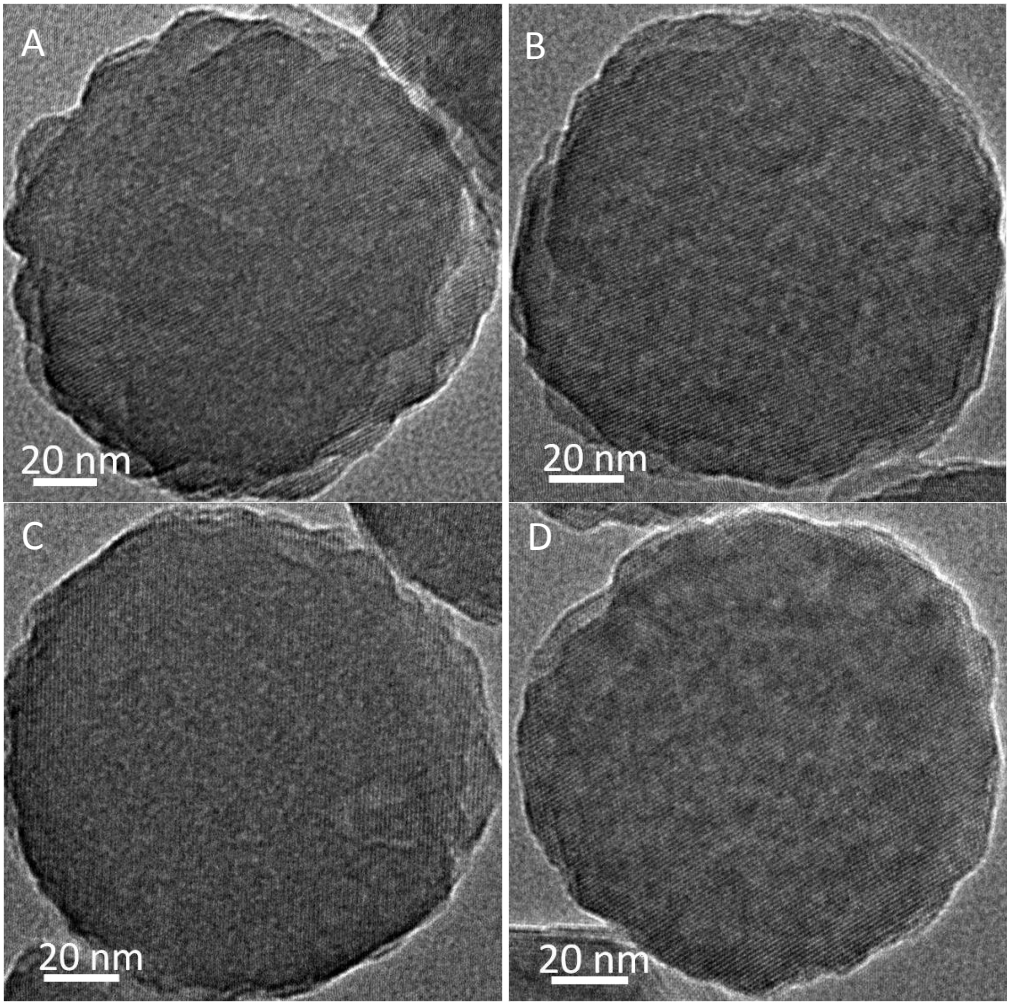

Figure S13. (A, B) TEM images of the sample HCN-ZSM-5 prepared under the same condition for HCN-ZSM-5-100/10d except using an original Si/Al ratio of **150**. (C, D) TEM images of the sample HCN-ZSM-5 prepared under the same condition for HCN-ZSM-5-100/10d except using an original Si/Al ratio of **300**. Similar small intracrystalline mesopores (2.2 nm) can be clearly observed inside every nanosized crystal, confirming that HCN-ZSM-5 can be obtained using an original Si/Al ratio of 150-300.

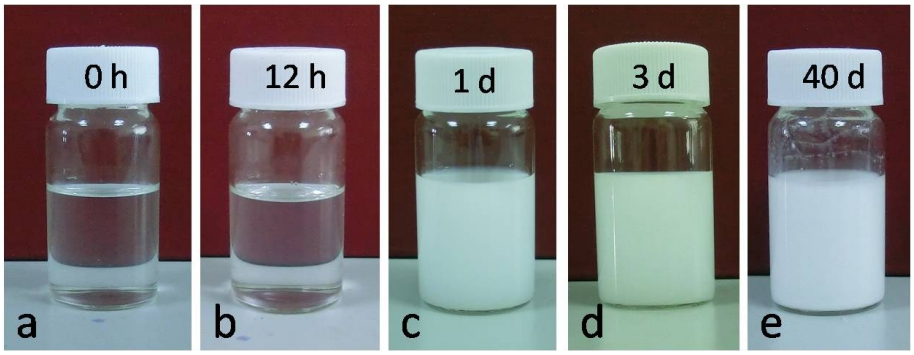

Figure S14. Photographs of HCN-ZSM-5-100/t samples milk-like colloid aqueous obtained at

different crystallization time: (a) 0 h, before crystallization at 100 ℃, (b) 12 h, (c) 1 d, (d) 3 d and (e) 40 d.

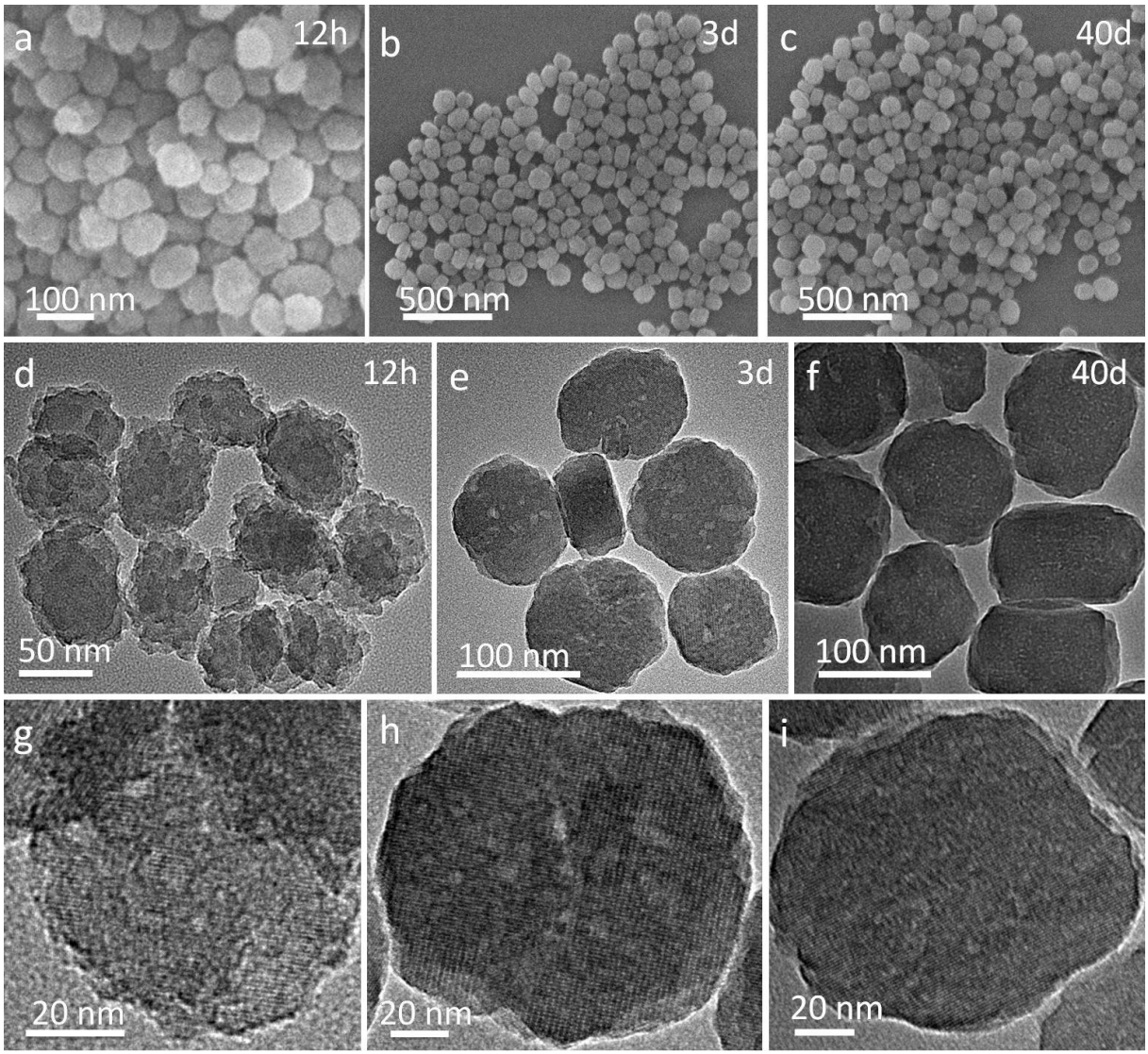

Figure S15. SEM and TEM images of the samples HCN-ZSM-5-100/t obtained at different crystallization time: (a, d) 12h, (b, e) 3d, (c, f) 40d.

The SEM the TEM images (Fig.S15a, d) reveal that every ZSM-5 nanocrystal is actually an aggregation composed of several 8-10 nm nanoblocks. Lattice fringes with consistent orientations over the entire particle region, but some broken by disordered mesopore structures, are clearly observed in the HRTEM image (Fig.S15g), suggesting a single crystal structure of the sample.

From the TEM images of the sample HCN-ZSM-5-100/3d crystallized for 3 days (Fig.S15e, h), it is seen that there are no nanoblocks but several holes are present in every nanosized crystal. With further crystallization (10 days or longer time), the holes disappear and a disordered mesopore structure of 2.2 nm becomes more and more prominent (Fig.S15f, i). According to the nitrogen sorption analysis (Fig.S18), a mesopore of 4.3 nm resulting from the aggregation of nanoblocks and a mesopore of 9 nm were ordinally present in the samples HCN-ZSM-5-100/12h and HCN-ZSM-5-100/3d, whereas only the mesopore of 2.2 nm, generated from growth defects,

were observed in the samples that were crystallized for at least 10 days. These results further confirm the process of growth-dissolution-regrowth.

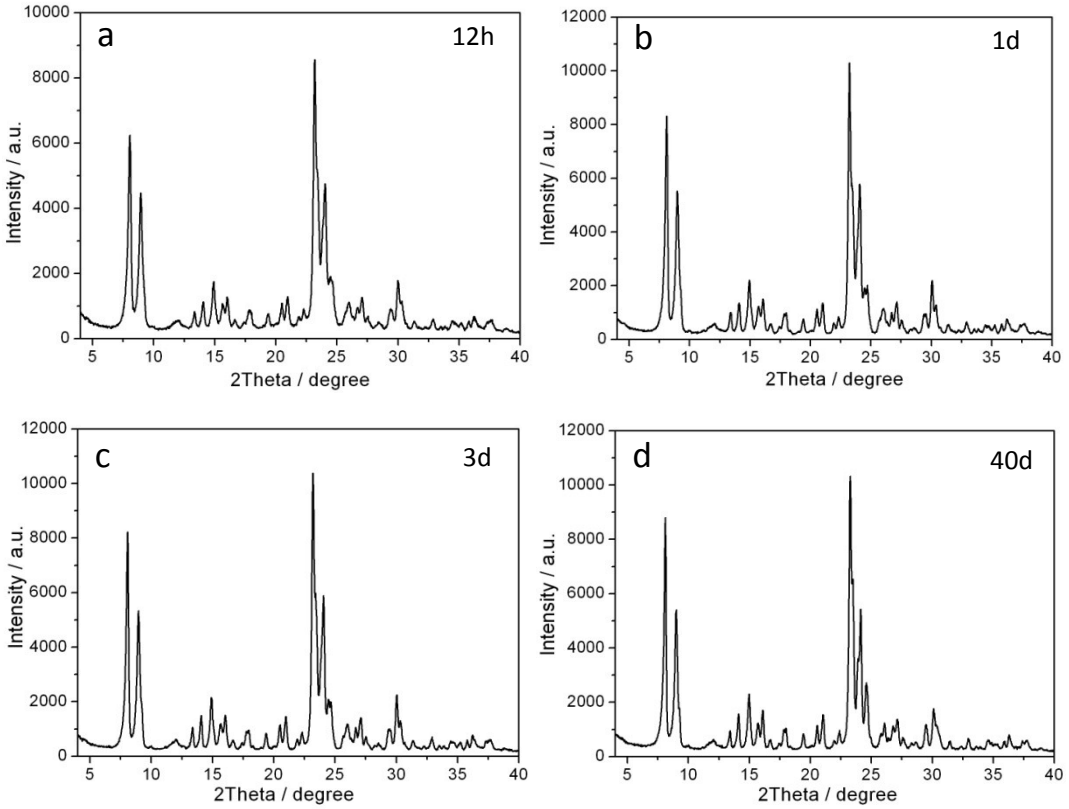

Figure S16. PXRD patterns of HCN-ZSM-5-100/t samples obtained at different crystallization time: (a) 12h, (b) 1d, (c) 3d and (d) 40d.

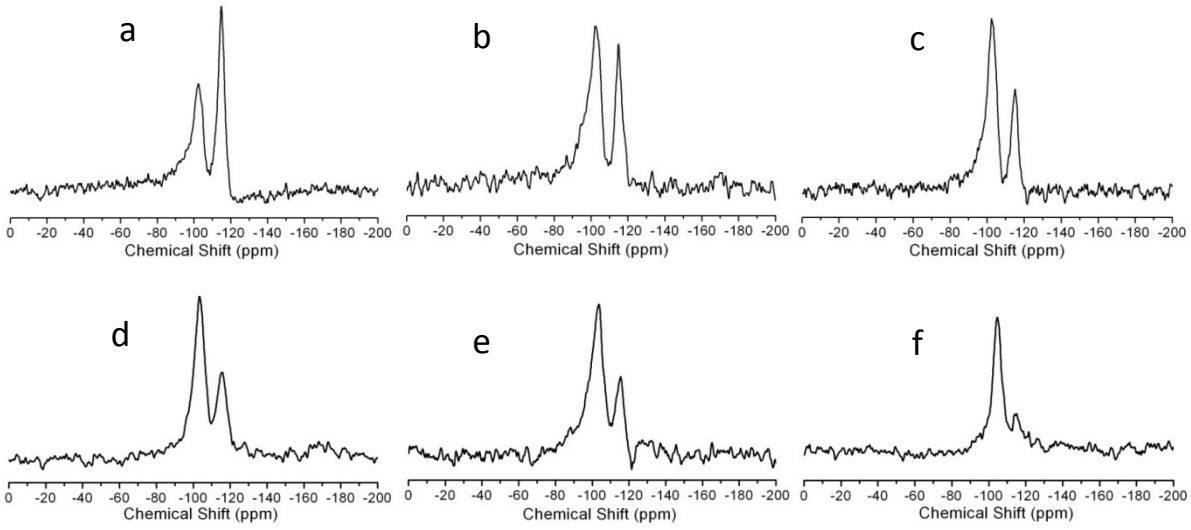

Figure S17. Solid state ^{29}Si NMR spectra of calcined HCN-ZSM-5-100/t samples obtained at different crystallization time: (a) 12 h, (b) 1 d, (c) 3d, (d) 10 d, (e) 40 d and (f) 190 d.

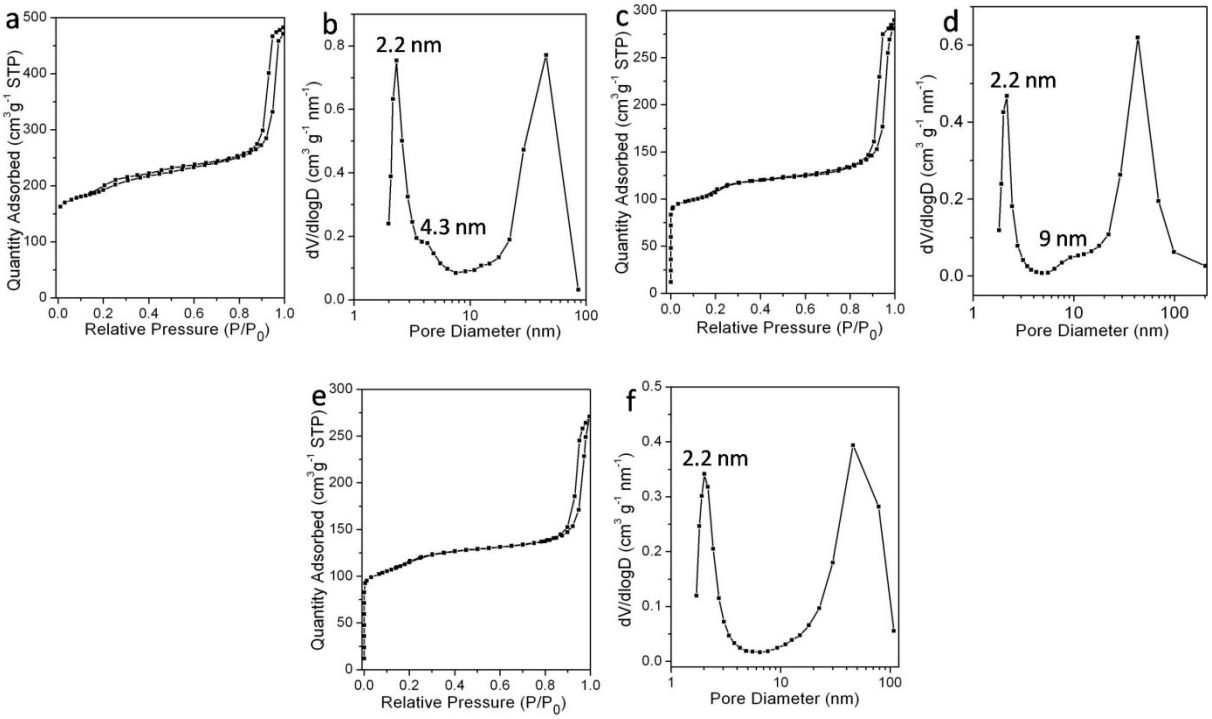

Figure S18. N_2 sorption isotherms and pore size distribution curves of calcined HCN-ZSM-5-100/t samples obtained at different crystallization time: (a, b) 12 h, (c, d) 3 d and (e, f) 40 d.

Table S1 Textural Properties of nanosized ZSM-5 samples prepared using different Si/Al ratios under different crystallization conditions in the current system.

Sample	Molar Composition	Crystallization Conditions	Crystallin e Yield	Micropore Surface Area	External Surface Area	BET Surface Area	Total Pore Volume
HCN-ZSM-5-100/12h	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, 12h	5 %	323 m^2/g	302 m^2/g	625 m^2/g	0.71 m^3/g
HCN-ZSM-5-100/1d	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, 1d	58 %	217 m^2/g	129 m^2/g	346 m^2/g	0.40 m^3/g
HCN-ZSM-5-100/3d	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, 3d	60 %	163 m^2/g	**203 m^2/g**	366 m^2/g	0.42 m^3/g
As-made HCN-ZSM-5-100/3d	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, 3d	60 %	9 m^2/g	26 m^2/g	35 m^2/g	0.24 m^3/g
HCN-ZSM-5-100/6d	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, 6d	60 %	291 m^2/g	139 m^2/g	430 m^2/g	0.47 m^3/g
HCN-ZSM-5-100/10d	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	**Si/Al:198 100℃, 10d**	62 %	186 m^2/g	**242 m^2/g**	428 m^2/g	0.44 m^3/g
As-made HCN-ZSM-5-100/10d	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, 10d	62 %	3 m^2/g	30 m^2/g	33 m^2/g	0.28 m^3/g
HCN-ZSM-5-100/20d	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, 20d	62 %	244 m^2/g	180 m^2/g	424 m^2/g	0.44 m^3/g
HCN-ZSM-5-100/40d	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, 40d	62 %	174 m^2/g	214 m^2/g	388 m^2/g	0.38 m^3/g
HCN-ZSM-5-100/190d	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, 190d	62 %	193 m^2/g	225 m^2/g	418 m^2/g	0.42 m^3/g
HCN-ZSM-5 -100/3d-**0.5TPA**	25SiO_2:0.0625Al_2O_3:0.1Na_2O: **5.5**TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, **3d**	83 %	318 m^2/g	**235 m^2/g**	**553 m^2/g**	0.44 m^3/g
HCN-ZSM-5 -100/10d-**0.5TPA**	25SiO_2:0.0625Al_2O_3:0.1Na_2O: **5.5**TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, **10d**	83 %	246 m^2/g	**268 m^2/g**	**514 m^2/g**	0.52 m^3/g
Micro-ZSM-5 -**0.3TPA**	25SiO_2:0.0625Al_2O_3:0.1Na_2O: **3.7**TPAOH:426.5H_2O:100EtOH	Si/Al:198 100℃, **3d**	90 %	-	-	-	-
HCN-ZSM-5-**160**/12h	25SiO_2:0.0625Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	Si/Al:198 **160℃, 12h**	90 %	181 m^2/g	175 m^2/g	356 m^2/g	0.35 m^3/g
Nano-Silicate-1	25SiO_2:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	**No Al** 100℃, 3d	50 %	258 m^2/g	78 m^2/g	336 m^2/g	0.45 m^3/g
Nano-ZSM-5-60	25SiO_2:**0.2083**Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	**Si/Al:60** 100℃, 3d	13 %	297 m^2/g	150 m^2/g	447 m^2/g	0.55 m^3/g
No Zeolite Crystals	25SiO_2:**0.2777**Al_2O_3:0.1Na_2O: 11TPAOH:426.5H_2O:100EtOH	**Si/Al:45** 100℃, 3d	-	-	-	-	-
HCN-ZSM-5	25SiO_2:0.0625Al_2O_3:0.1Na_2O:	Si/Al:198	91 %	150 m^2/g	212 m^2/g	362 m^2/g	0.32 m^3/g

-160/12h-0.5TPA	**5.5**TPAOH:426.5H_2O:100EtOH	**160℃, 12h**					
HCN-ZSM-5 **-160/7d-0.5TPA**	25SiO_2:0.0625Al_2O_3:0.1Na_2O: **5.5**TPAOH:426.5H_2O:100EtOH	Si/Al:198 **160℃, 7d**	91 %	214 m^2/g	80 m^2/g	294 m^2/g	0.35 m^3/g

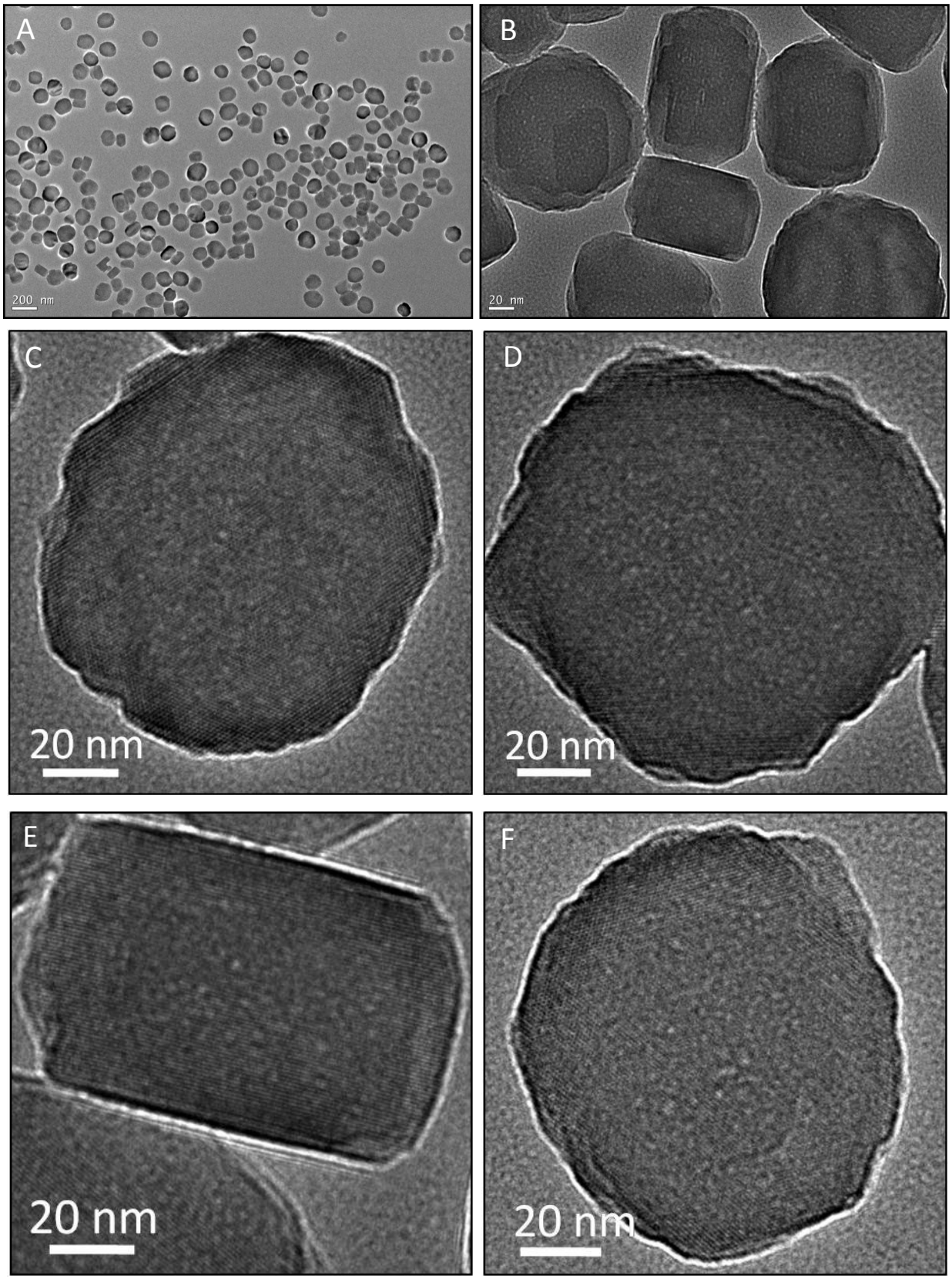

Figure S19. (A, B) TEM images of HCN-ZSM-5-100/190d sample crystallized at 100 ℃ for 190 d. (C, D, E, F) The relevant individual nanocrystal with different crystal lattice plane.

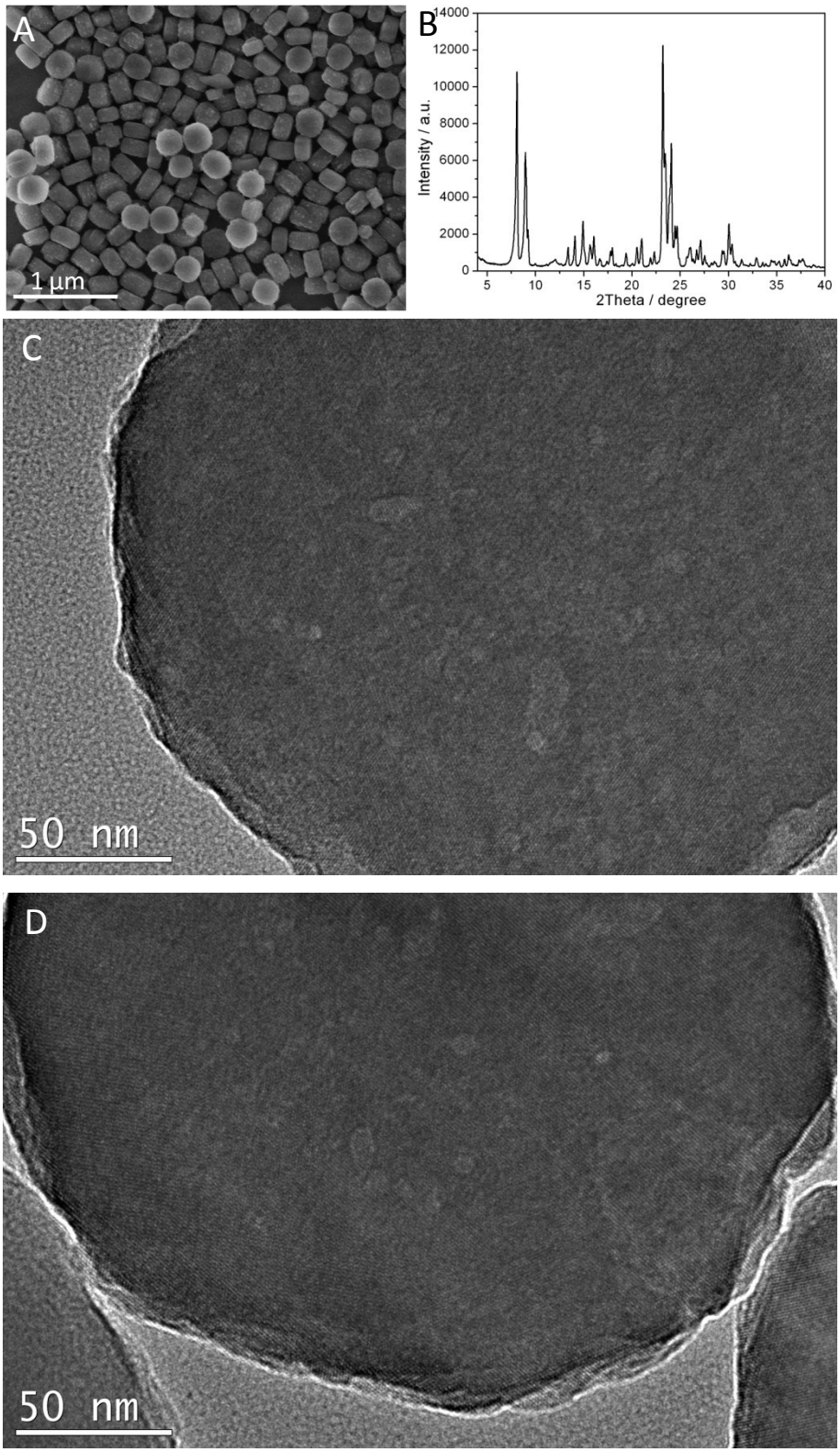

Figure S20. SEM image (A), XRD pattern (B) and HRTEM images (C, D) with different crystal

lattice plane of the sample HCN-ZSM-5-160/7d crystallized at 160 ℃ for 12 h. The ratio of TPA/Si is 5.5/25. The composition is 25SiO_2: 0.0625Al_2O_3: 0.1Na_2O: **5.5**TPAOH: 426.5H_2O: 100EtOH.

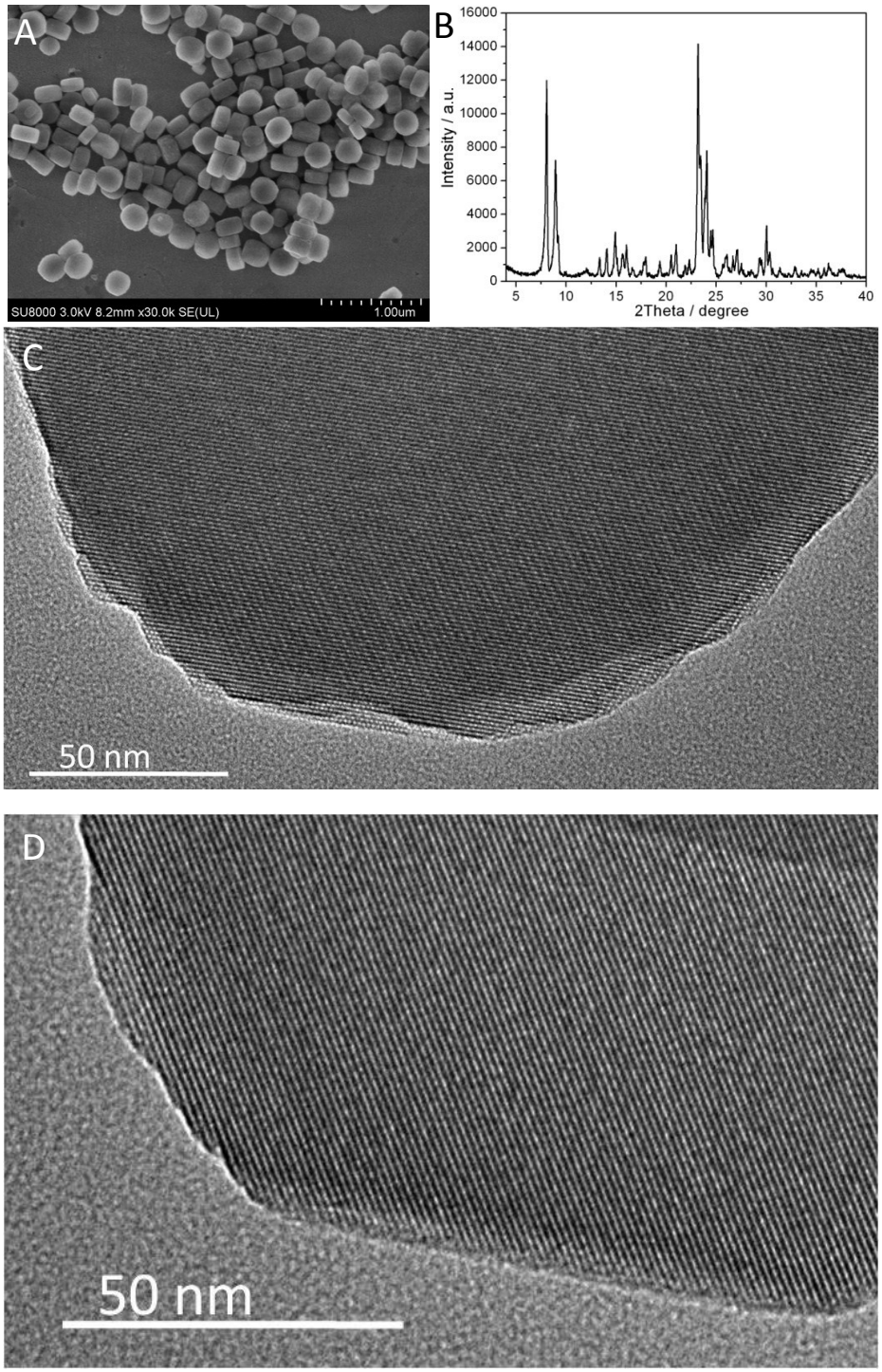

Figure S21. SEM image (A), XRD pattern (B) and HRTEM images (C, D) with different crystal lattice plane of the HCN-ZSM-5-160/7d sample crystallized at 160 ℃ for 7 d. The ratio of TPA/Si

is 5.5/25. The composition is $25SiO_2$: $0.0625Al_2O_3$: $0.1Na_2O$: **5.5**TPAOH: $426.5H_2O$: 100EtOH.

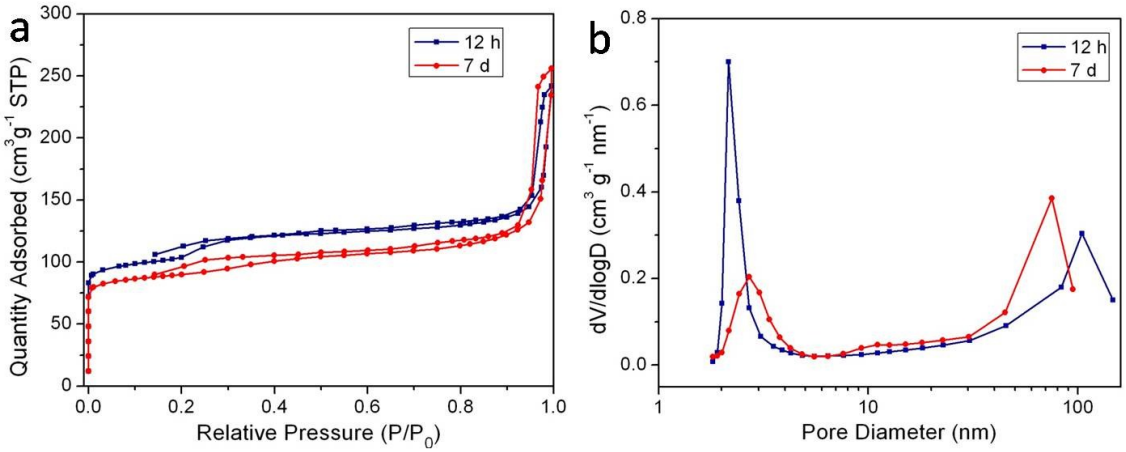

Figure S22. N_2 sorption isotherms (a) and pore size distribution curves (b) of the samples in Figure.S20, 21.

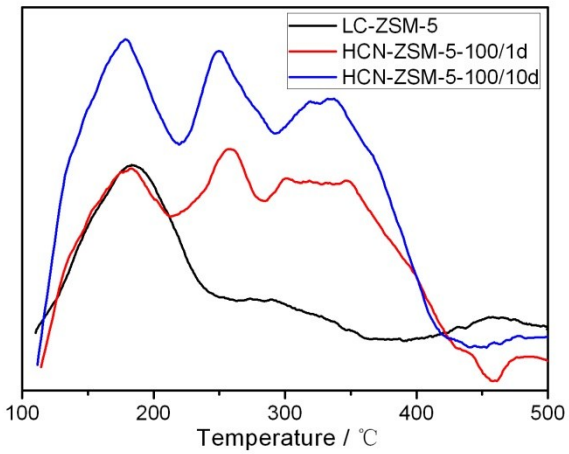

Figure S23. NH_3 TPD profiles of the sample LC-ZSM-5, HCN-ZSM-5-100/1d and HCN-ZSM-5-100/10d.

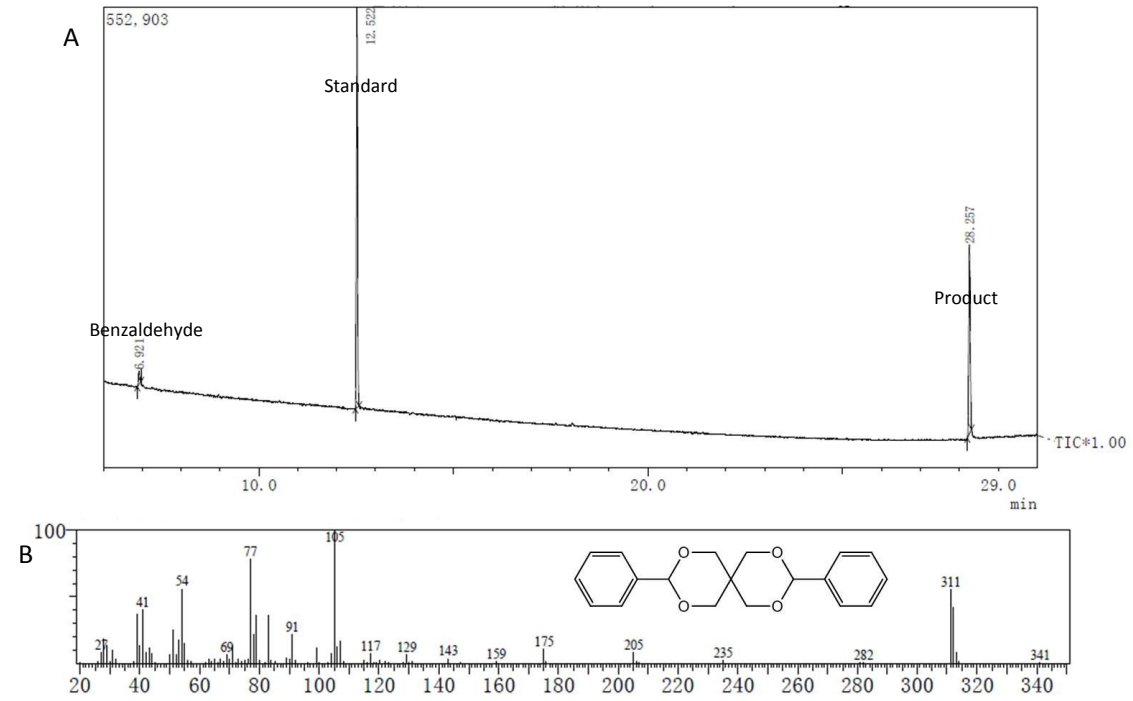

Figure S24. (A) Gas chromatography-mass spectrum of PBP catalytic reaction mixture; (B) Mass spectrum of target product. The target product with the selectivity of nearly 100 % can be clearly identified from these spectra.

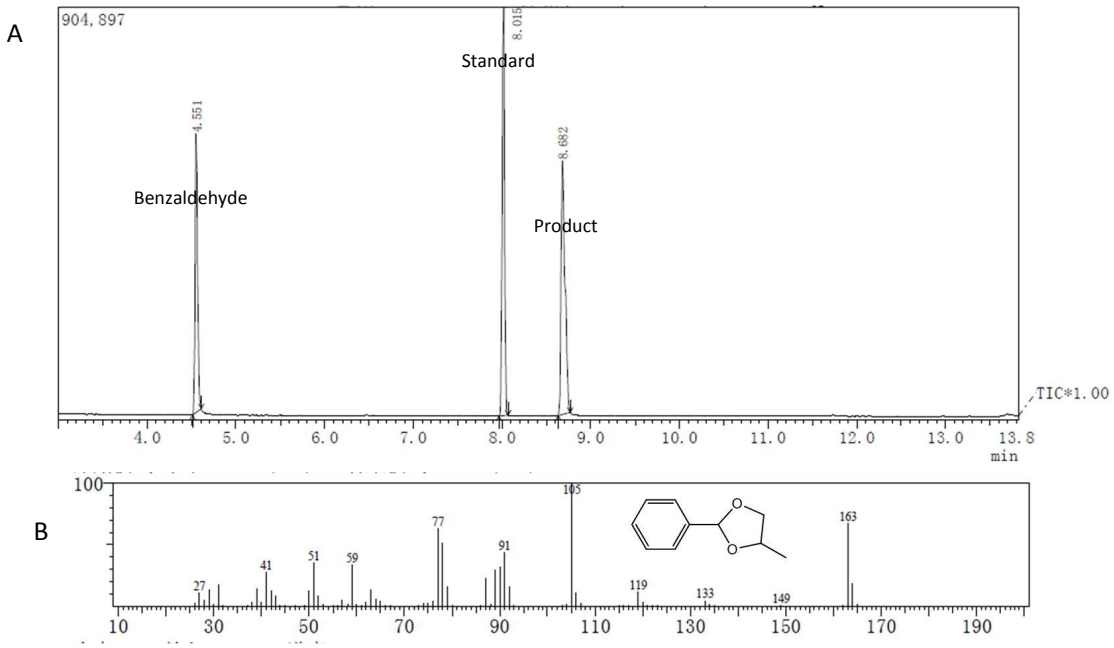

Figure S25. (A) Gas chromatography-mass spectrum of BPG catalytic reaction mixture; (B) Mass spectrum of target product. The target product with the selectivity of nearly 100 % can be clearly identified from these spectra.

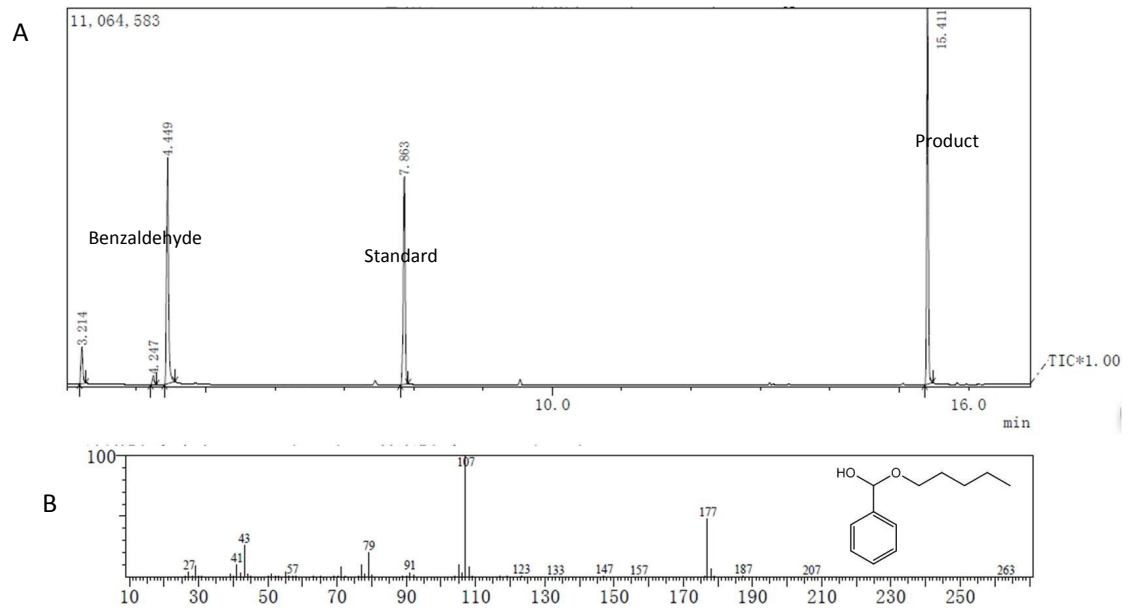

Figure S26. (A) Gas chromatography-mass spectrum of CBP catalytic reaction mixture; (B) Mass spectrum of target product. The target product with the selectivity of nearly 100 % can be clearly identified from these spectra.

References

(1) Wang, R.; Liu, W.; Ding, S.; Zhang, Z.; Li, J.; Qiu, S. Chem. Commun. **2010**, 46, 7418-7420.