

Supporting Information for

Controllable fabrication of single-crystalline, ultrafine and high-silica hierarchical ZSM-5 aggregates via solid-like state conversion

Hongyao Li,* Yaquan Wang, Fanjun Meng, Fei Gao, Chao Sun, Chunyang Fan, Xiao Wang, Shuhai Wang

Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.

*Corresponding author: Tel.: +86-22-23507881; Fax: +86-22-23507881; E-mail address : lhy0501@163.com

Table of Contents

Tables.....S2

FiguresS3

1. Tables

Table S1 Synthesis conditions and textural properties of zeolite samples.

Sample	SiO ₂ /Al ₂ O ₃	Seed/SiO ₂	HTAB/SiO ₂	RC ¹ [%]	S _{ext} ² (m ² g ⁻¹)	S _{int} ² (m ² g ⁻¹)	V _{meso} ² (cm ³ g ⁻¹)	V _{meso} ² (cm ³ g ⁻¹)	V _{meso} ² (cm ³ g ⁻¹)
HA-167-2S-5H	167	0.02	0.05	107	409	201	0.1	0.29	0.19
HA-200-2S-5H	200	0.02	0.05	108	406	213	0.09	0.27	0.18
HA-250-2S-5H	250	0.02	0.05	109	399	229	0.08	0.25	0.17
HA-313-2S-5H	313	0.02	0.05	110	399	225	0.08	0.24	0.16
HA-167-0.5S-5H	167	0.005	0.05	212	393	117	0.13	0.25	0.12
HA-167-2S-5H	167	0.02	0.05	107	409	201	0.1	0.29	0.19
HA-167-4S-5H	167	0.04	0.05	106	410	157	0.12	0.27	0.15
HA-167-6S-5H	167	0.06	0.05	212	418	143	0.13	0.29	0.16
HA-167-2S-1H	167	0.02	0.01	81	266	100	0.08	0.23	0.15
HA-167-2S-3H	167	0.02	0.03	100	378	202	0.09	0.24	0.15
HA-167-2S-5H	167	0.02	0.05	107	409	201	0.1	0.29	0.19
HA-167-2S-7H	167	0.02	0.07	102	388	180	0.10	0.23	0.13
C-ZSM-5	167	0.02	0	100	311	167	0.06	0.22	0.16
C ₁ -ZSM-5	167	-----	-----		330	147	0.07	0.20	0.13

Table S2 NH₃-TPD results of the selected samples.

Sample	Weak acid	Strong acid	Total acid	Strong/Weak
	(mmol NH ₃ per g cat.)	(mmol NH ₃ per g cat.)	(mmol NH ₃ per g cat.)	
HA-167-2S-5H	0.097	0.128	0.225	1.32
HA-167-2S-7H	0.116	0.125	0.241	1.08
C-ZSM-5	0.163	0.134	0.297	0.82
C ₁ -ZSM-5	0.055	0.146	0.201	2.65

Table S3 Acidity of the ZSM-5 zeolites determined by Py-IR spectroscopy at 25 °C.

Zeolite	B acid	L acid	B/L
	(a.u.)	(a.u.)	
HA-167-2S-5H	0.117	0.0109	10.7
HA-167-2S-7H	0.113	0.0120	9.4
C-ZSM-5	0.106	0.0277	3.8
C ₁ -ZSM-5	0.103	0.0430	2.4

Brønsted and Lewis acidities were quantified according to the integrated areas of the absorbance peaks at 1539 and at 1448 cm⁻¹, respectively.

Table S4 Product distribution of MTP reaction over the HA-167-2S-5H, HA-167-2S-7H, C-ZSM-5 and C₁-ZSM-5 catalysts measured at steady state condition.

Catalyst	Conversion (%)	Selectivity (C-mol.%)					C ₂ ^a -C ₄ ^a	P/E
		C ₁ - ^a	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	C ₅ ^b		
HA-167-2S-5H	100	3.7	5.5	40.1	22.9	27.8	68.5	7.3
HA-167-2S-7H	100	2.9	5.3	40.3	22.9	28.6	68.5	7.6
C-ZSM-5	99.3	5.3	11.1	33.1	17.2	33.3	61.4	3.0
C ₁ -ZSM-5	99.0	4.6	5.9	38.7	21.4	29.4	66.0	6.6
C ₂ -ZSM-5	99.6	6.1	9.9	31.9	17.9	34.6	59.7	3.2

a C₁-C₄ saturated hydrocarbons.

b C₅ and higher hydrocarbons.

Table S5. The textural properties of HA-ZSM-5 samples synthesized at different crystallization times.

crystallization times (h)	RC ^a [%]	S _{BET} ^b (cm ² g ⁻¹)	S _{ext} ^c (cm ² g ⁻¹)	V _{micro} ^d (cm ³ g ⁻¹)	V _{poro} ^e (cm ³ g ⁻¹)	V _{meso} ^f (cm ³ g ⁻¹)
6	0	119	104	0.006	0.99	0.98
12	0	121	102	0.007	0.91	0.90
18	0	124	94	0.01	0.65	0.64
24	61	168	106	0.03	0.52	0.49
30	103	366	109	0.12	0.24	0.12
36	111	393	173	0.10	0.21	0.11

2. Figures

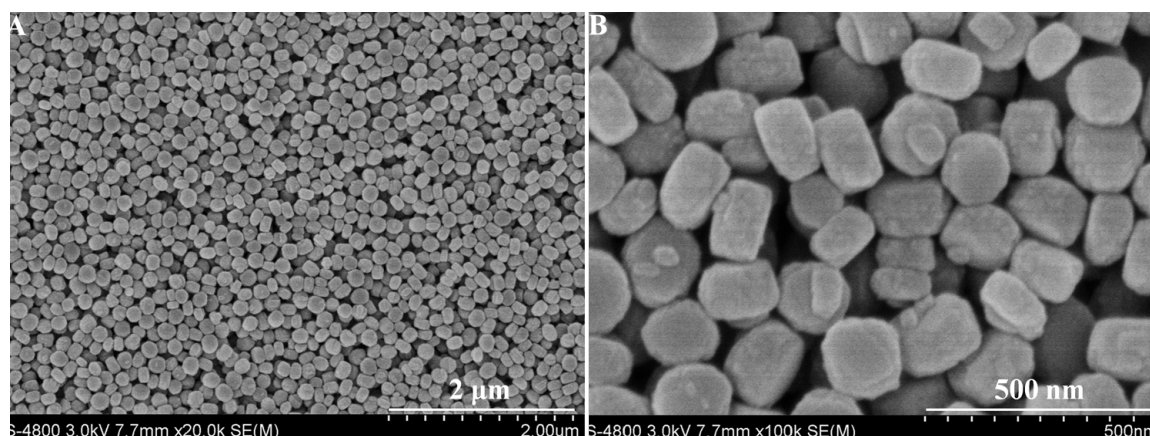


Fig. S1 SEM images for S-1 seeds (A) low magnification, (B) high magnification.

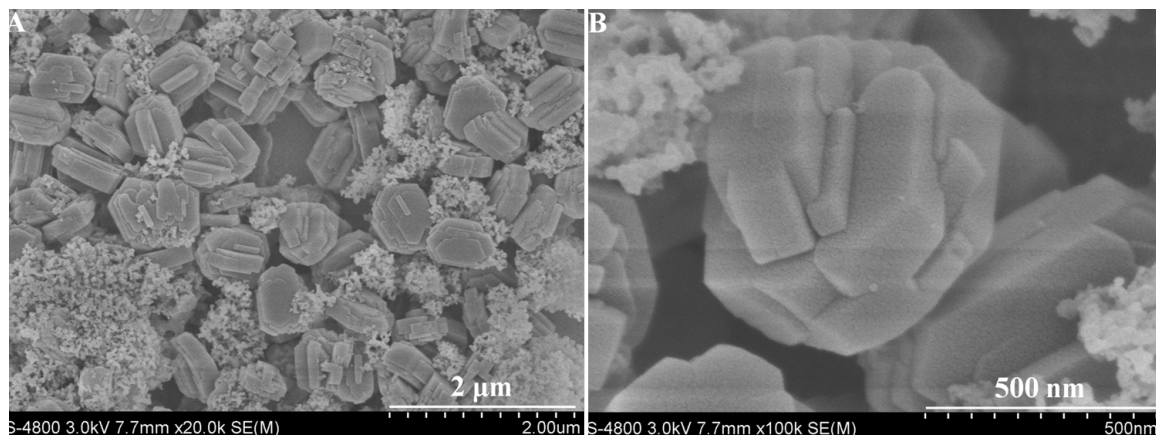


Fig. S2 SEM images for C-ZSM-5 zeolite (A) low magnification, (B) high magnification.

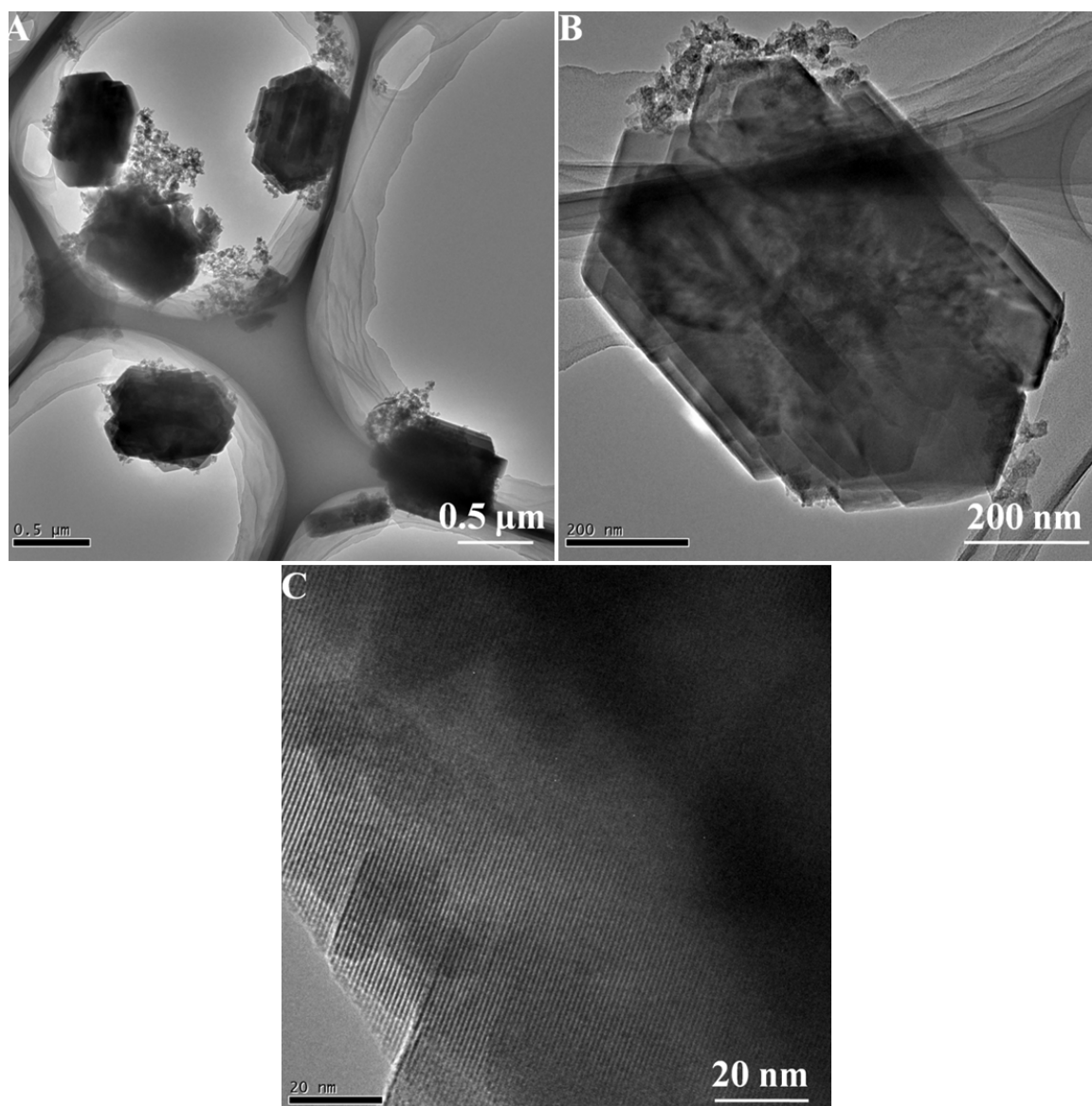


Fig. S3 TEM images for C-ZSM-5 zeolite (A) low magnification, (B) and (C) high magnification.

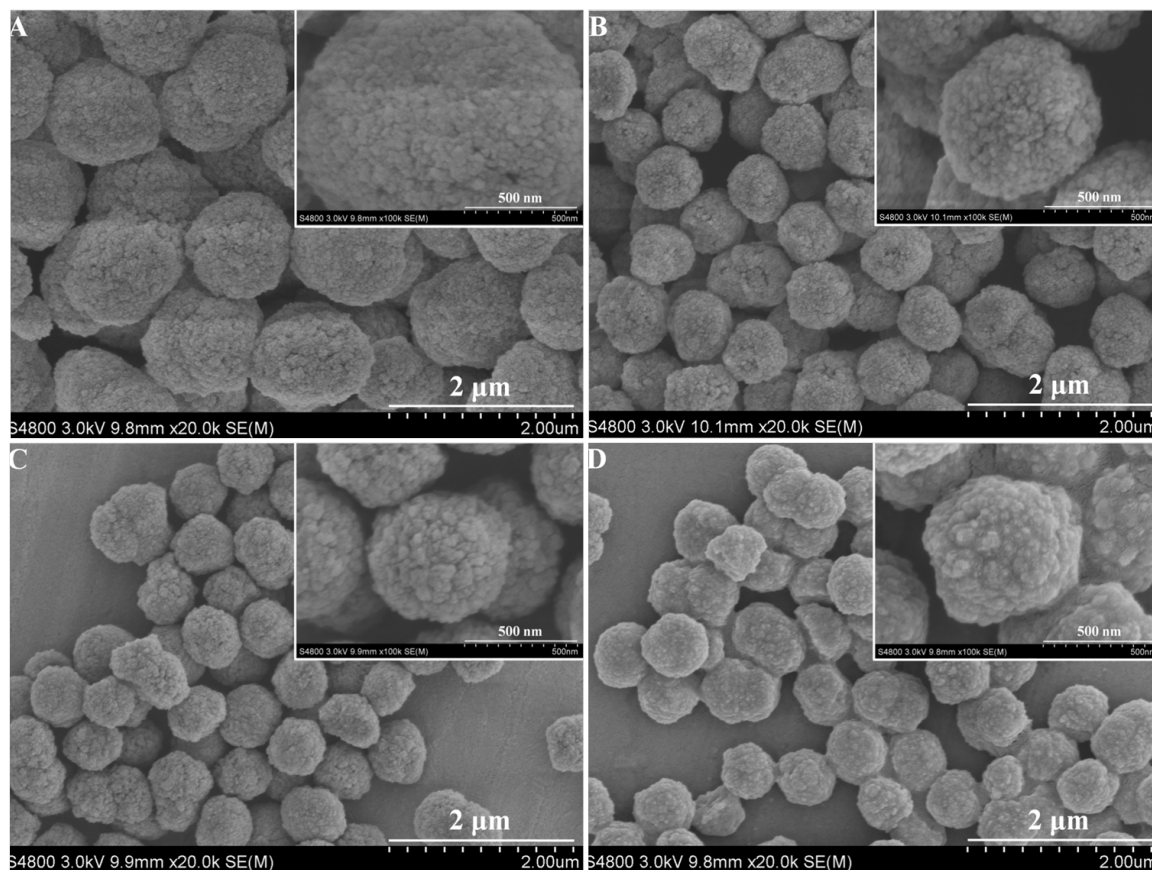


Fig. S4 SEM images of the HA-ZSM-5 zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios
(A) HA-167-2S-5H; (B) HA-200-2S-5H; (C) HA-250-2S-5H; (D) HA-313-2S-5H.

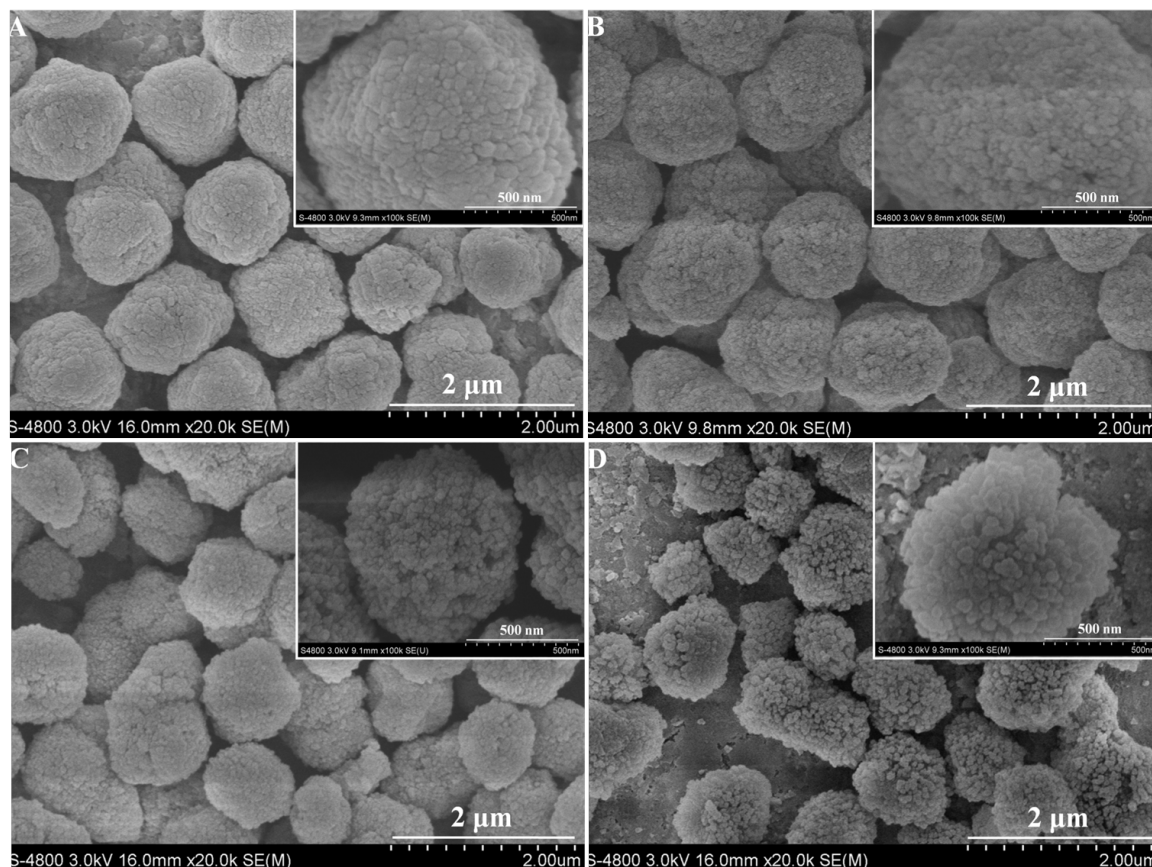


Fig. S5 SEM images of the HA-ZSM-5 zeolites with different Seed/ SiO₂ ratios
(A) HA-167-0.5S-5H; (B) HA-167-2S-5H; (C) HA-167-4S-5H; (D) HA-167-6S-5H.

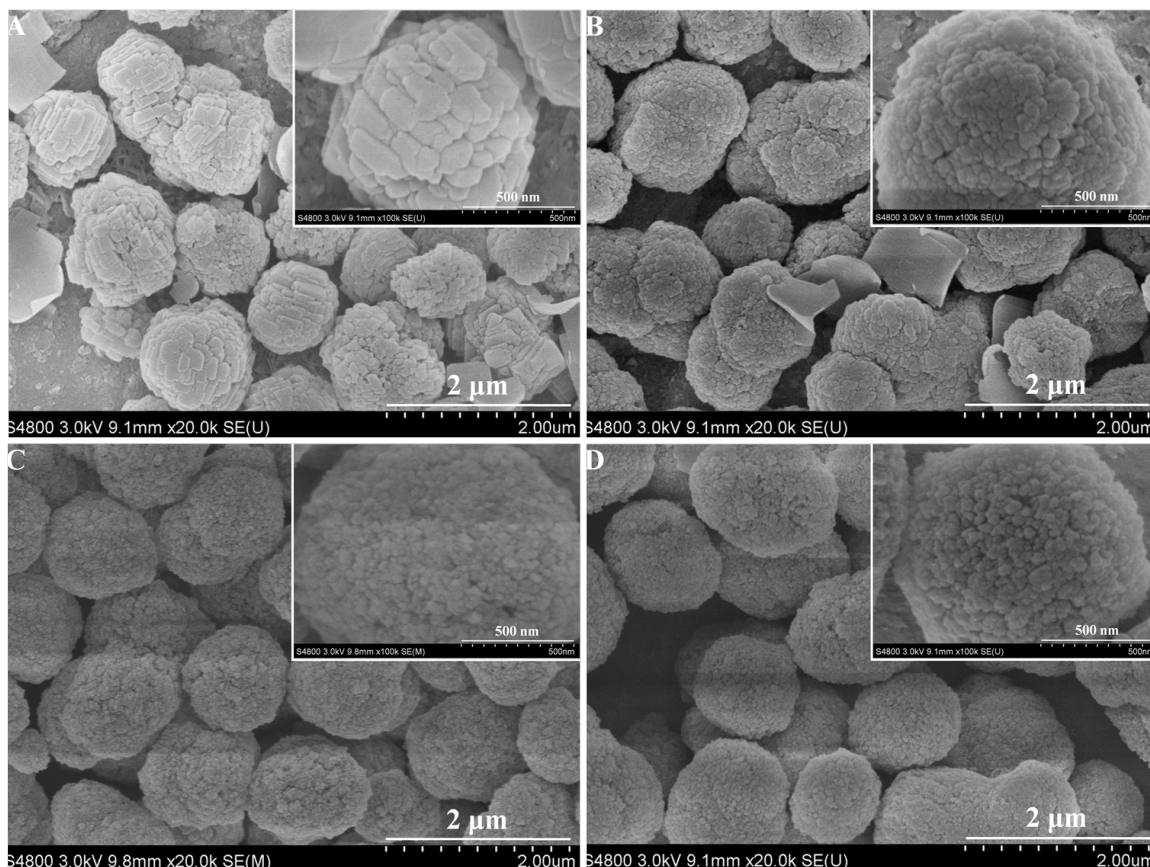


Fig. S6 SEM images of the HA-ZSM-5 zeolites with different HTAB/ SiO₂ ratios. (A) HA-167-2S-1H; (B) HA-167-2S-3H; (C) HA-167-2S-5H; (D) HA-167-2S-7H.

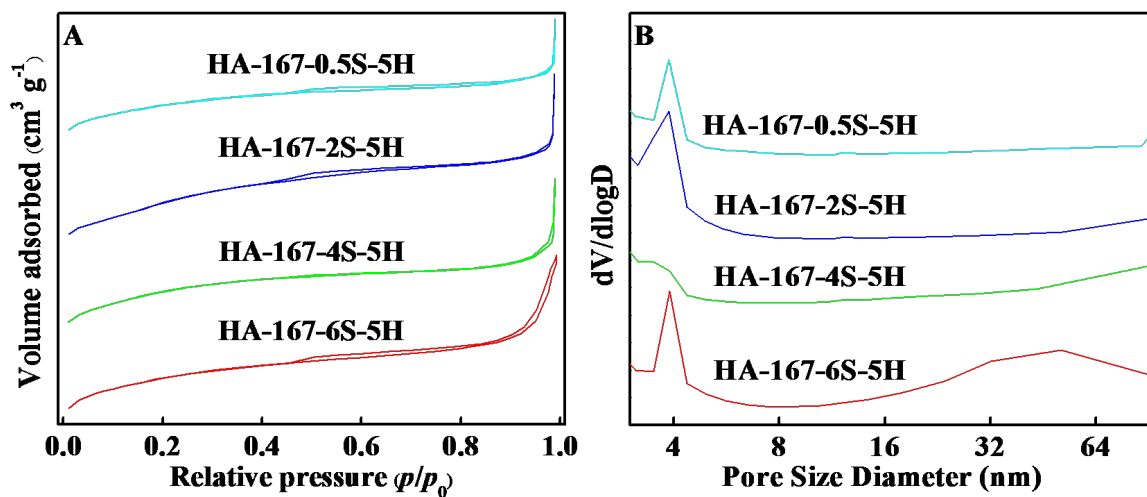


Fig. S7 N₂ adsorption-desorption isotherms (A) and PSD curves (B) of the HA-ZSM-5 zeolites prepared with different Seed/ SiO₂ ratios.

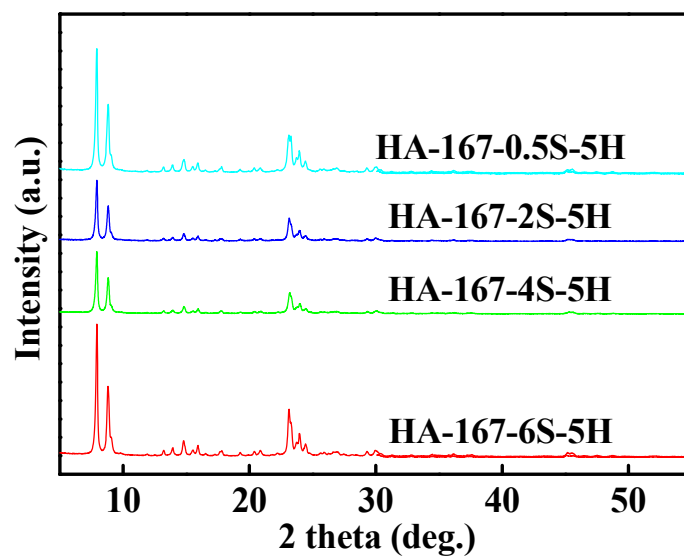


Fig. S8 XRD patterns of HA-ZSM-5 zeolites synthesized with different seed/SiO₂ ratios.

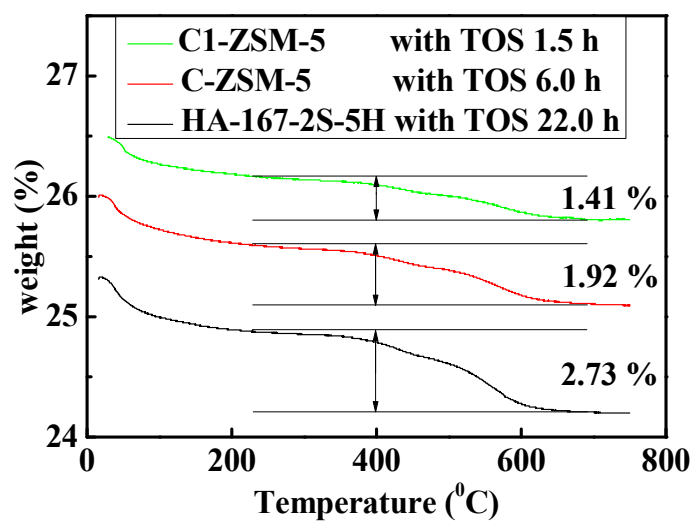


Fig. S9 TG curves of C₁-ZSM-5, C-ZSM-5 and HA-167-2S-5H catalysts in the MTP reaction test at 470 °C after deactivation.

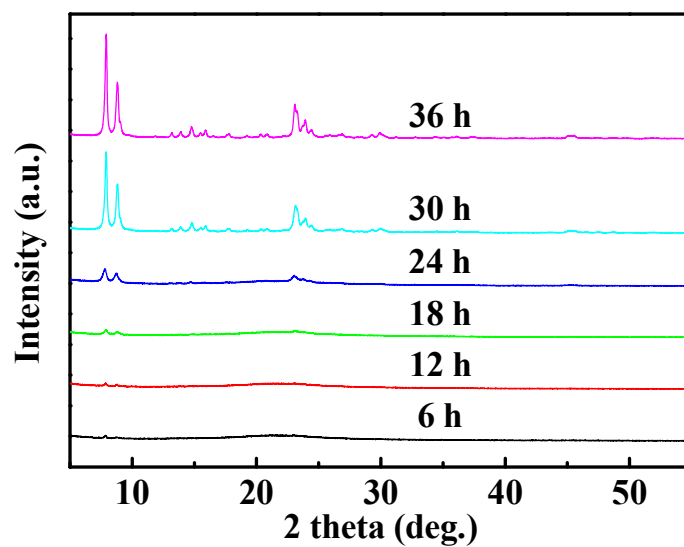


Fig. S10 The XRD patterns of HA-ZSM-5 samples prepared at different crystallization time.

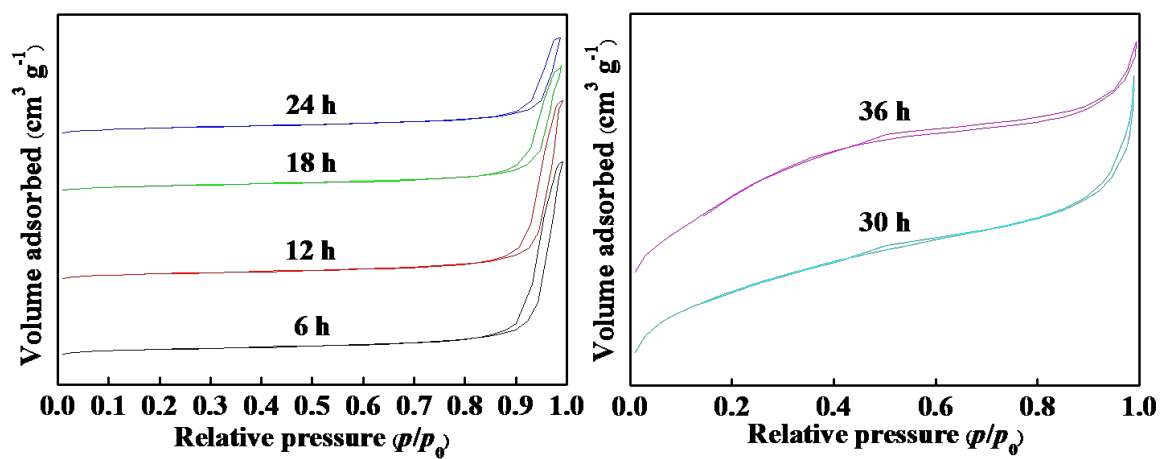


Fig.S11 N_2 adsorption-desorption isotherms of HA-ZSM-5 samples prepared at different crystallization times.

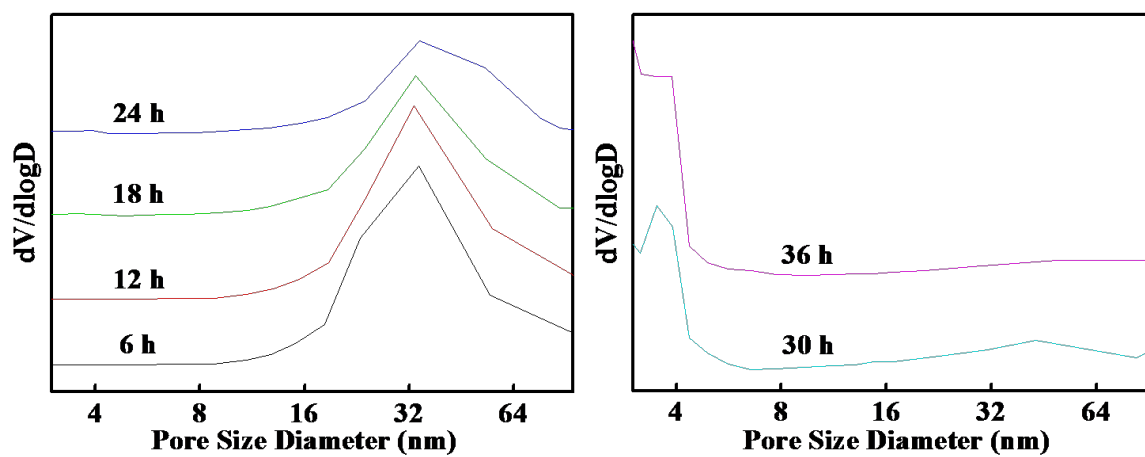


Fig.S12 Pore size distributions of HA-ZSM-5 samples prepared at different crystallization times.