Supporting Information

High-Efficiency Synthesis of Enhanced-Titanium and Anatase-Free TS-1 Zeolite by Using Crystallization Modifier

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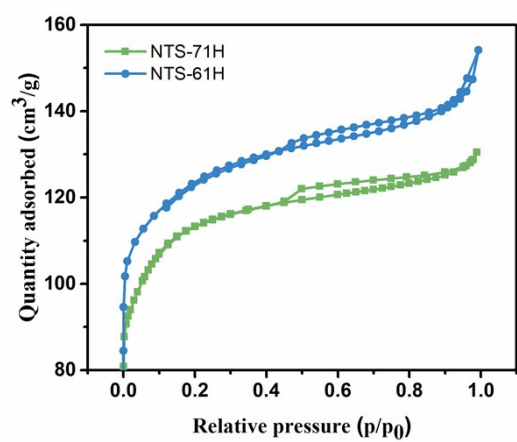
‡ Equally contributed to this work.

Fig. S1 N$_2$ adsorption–desorption isotherms of NTS-61H and NTS-73H.

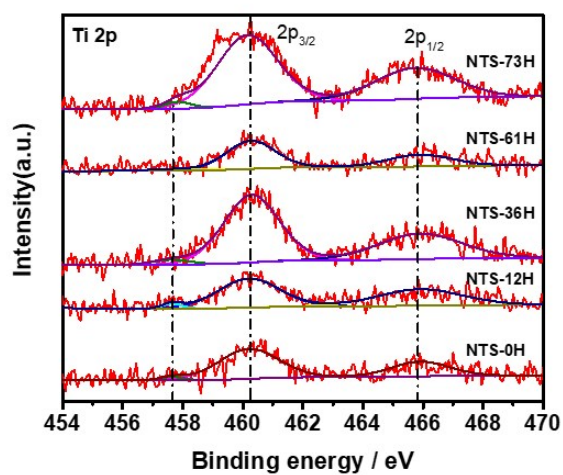Fig. S2 The XPS spectra of Ti 2p of NTS-0H, NTS-12H, NTS-36H, NTS-61H and NTS-73H.
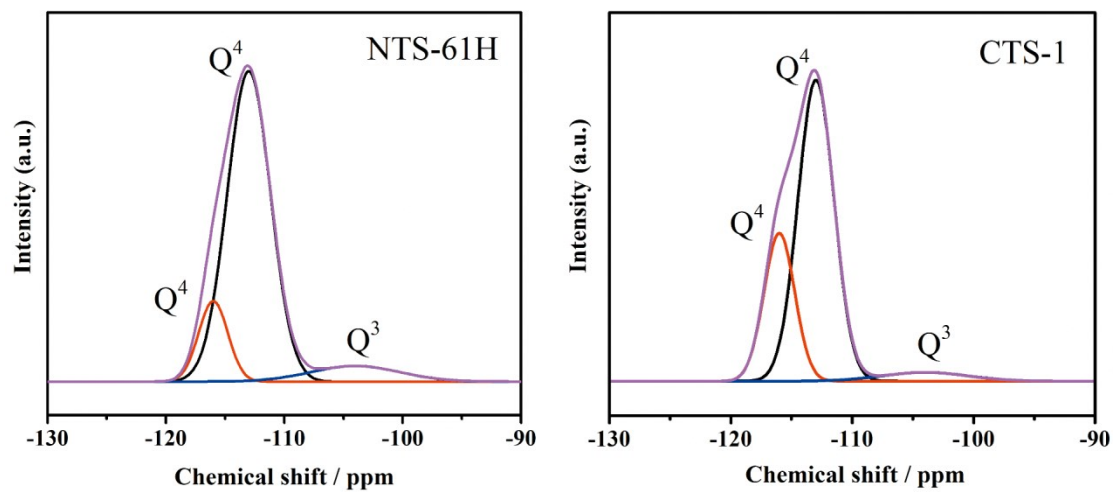
Fig. S3 ^{29}Si MAS NMR spectra of NTS-61H and CTS-1.
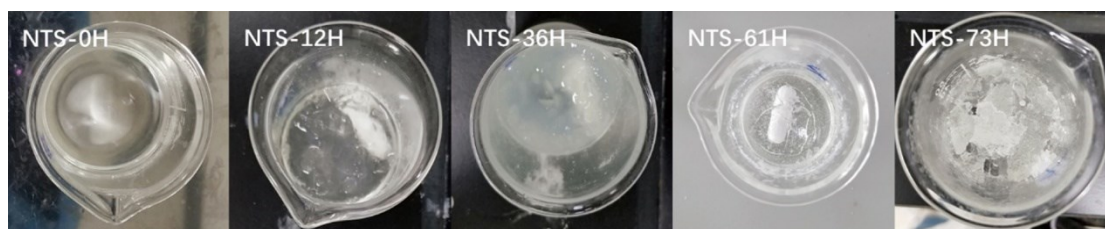
Fig. S4 Photos of initial synthetic mixtures with different amount of H$_3$BTC.
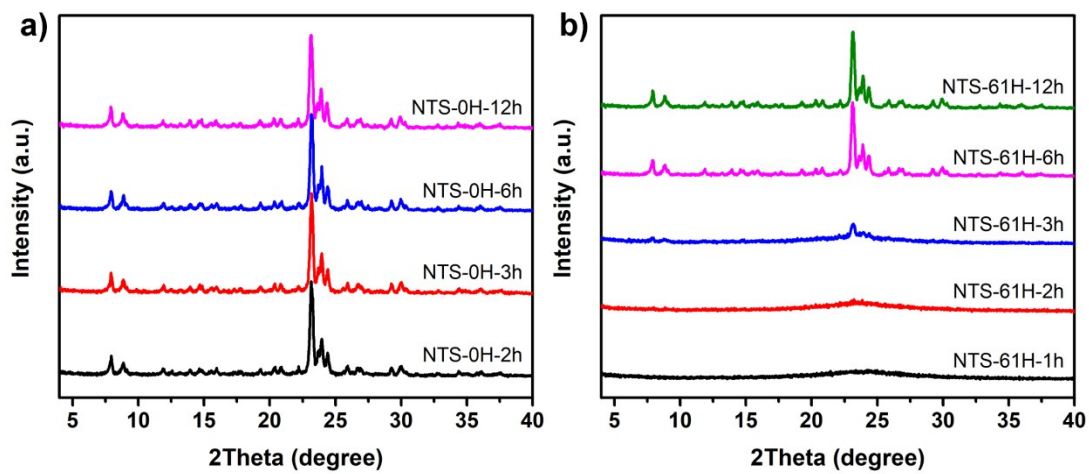
Fig. S5 XRD patterns of a) NTS-0H-xh samples and b) NTS-61H-xh samples.
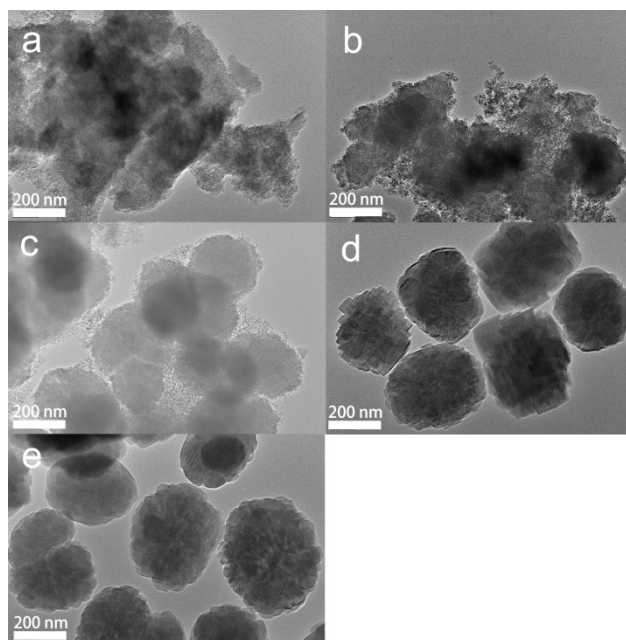
Fig. S6 TEM images of a) NTS-61H-1h, b) NTS-61H-2h, c) NTS-61H-3h, d) NTS-61H-6h, e) NTS-

61H-12h.
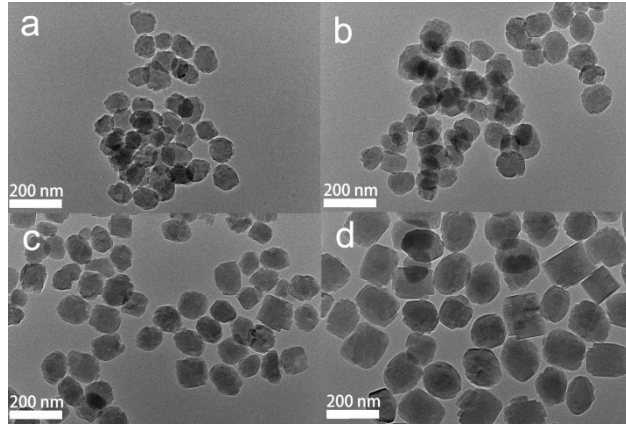
Fig. S7 TEM images of a) NTS-0H-2h, b) NTS-0H-3h, c) NTS-0H-6h, d) NTS-0H-12h.
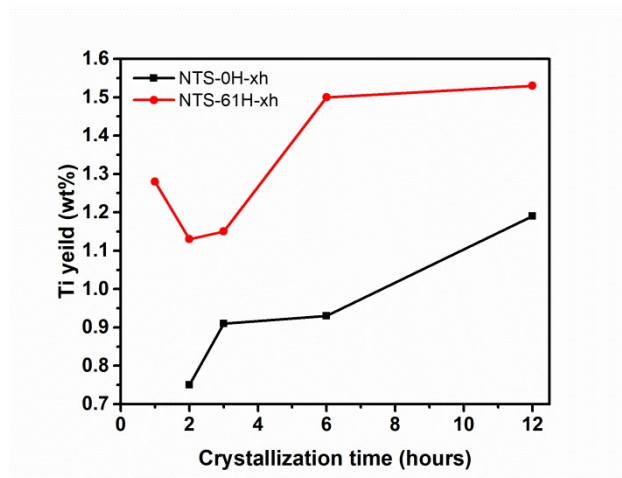
Fig. S8 Respective yields of Ti in NTS-0H-xh and NTS-61H-xh.

Fig. S9 UV-vis spectra of a) NTS-0H-xh and b) NTS-61H-xh.

Fig. S10 XRD patterns of a) CTS-yd samples and b) NTS-yd samples.
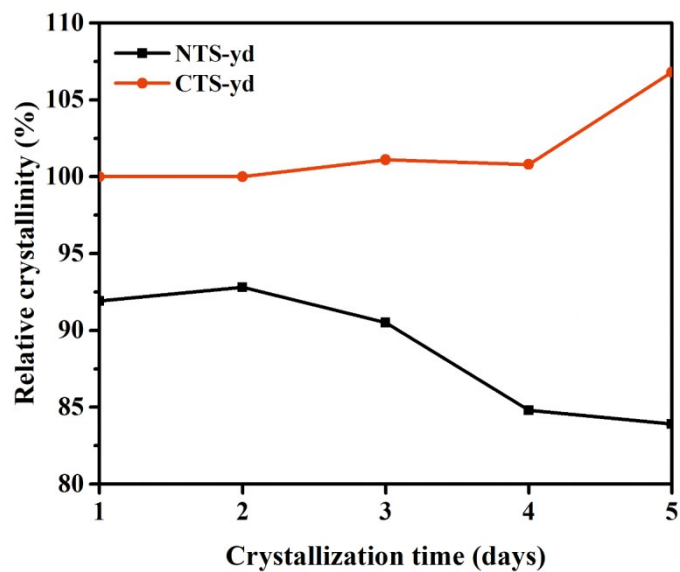
Fig. S11 Relative crystallinity curves of CTS-yd samples and NTS-yd samples (the crystallinity of CTS-1 as the standard 100%).
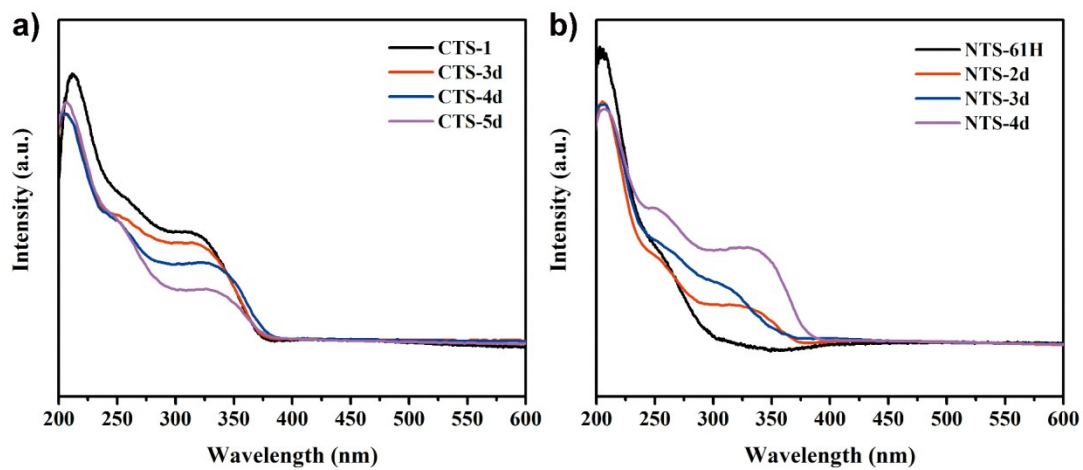
Fig. S12 UV-vis spectra of CTS-yd samples and NTS-yd samples.

Table S1 Textural properties of CTS-1 and synthesized TS-1 samples.

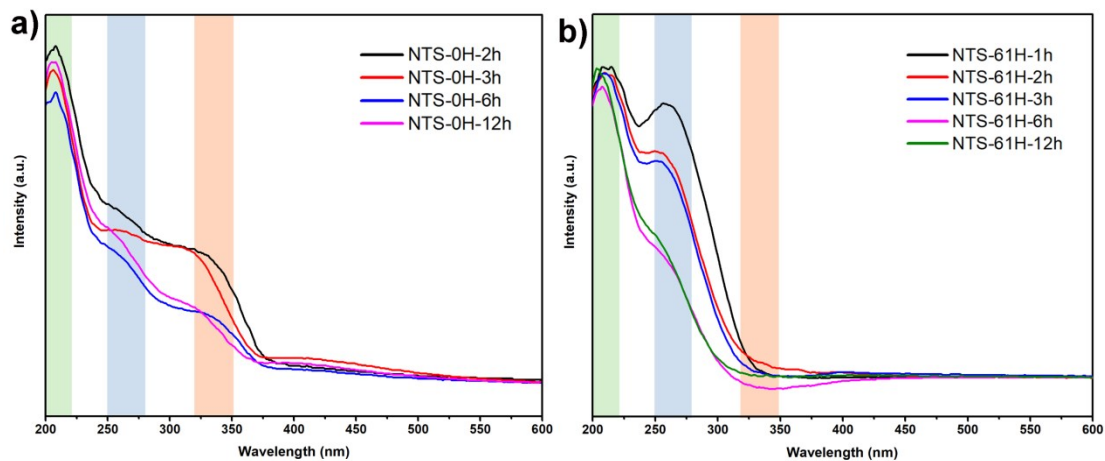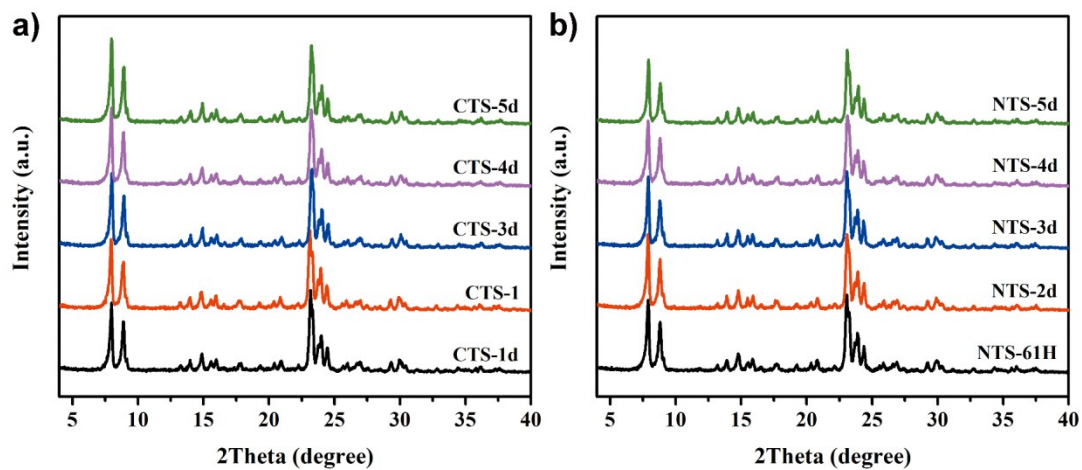|	S_{BET} (m^2 g^{-1}) [a]	S_{micro} (m^2 g^{-1}) [b]	S_{ext} (m^2 g^{-1}) [b]	V_{total} (cm^3 g^{-1}) [c]	V_{micro} (cm^3 g^{-1}) [d]	V_{meso} (cm^3 g^{-1}) [e]
CTS-1	385	278	108	0.24	0.13	0.11
NTS-0H	397	264	133	0.28	0.12	0.16
NTS-12H	391	221	169	0.46	0.12	0.34
NTS-36H	393	224	169	0.39	0.12	0.27
NTS-61H	358	230	128	0.24	0.13	0.11
NTS-73H	344	218	126	0.20	0.12	0.08

[a] Surface area was calculated from the nitrogen adsorption isotherm using the BET method.
[b] S_{micro} (micropore area), S_{ext} (external surface area) were calculated using the t-plot method.
[c] V_{total} (total pore volume) at P/P$_0$ = 0.99.
[d] V_{micro} (micropore volume) was calculated using the t-plot method.
[e] V_{meso} (mesopore volume) = V_{total} (total pore volume) - V_{micro}.

Table S2 Comparison of titanium-rich TS-1 synthesized by the hydrothermal methods.

Crystallization modifier	Synthetic method	Si/Ti	Ti wt%	Time-gel. (hours) [d]	Crystallization temperature (℃)	Time-cry. (days) [e]	Ref.
H_3BTC	Hydrothermal method	48.5 [a]		4.5	180	1	This work
$(NH_4)_2CO_3$	Hydrothermal method	65-66 [b]		>2.5	160	3	1
$(NH_4)_2CO_3$	Hydrothermal method and post-treatments	34 [a]			170	6	2
$(NH_4)_2CO_3$	Hydrothermal method and post-treatments	43.1 [a]		>4.5	170	6	3
PAA	Hydrothermal method	44 [a]		>0.5	170	7	4
IPA	Hydrothermal method		3.08-9.92 [c]	>8.5	170	7	5
Triton X-100	Rotation hydrothermal method	33.9 [a]		>8	170	4	6

[a] The elemental compositions in the bulk were determined by ICP; [b] Molar ratio of Si to Ti was determined by energy dispersive X-ray spectroscopy (EDS); [c] The percentage content of titanium in the catalysts was determined by XRF method; [d] Time of gel preparation; [e] Time of hydrothermal crystallization.

References

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4. J. Wang, Y. Zhao, T. Yokoi, J. N. Kondo and T. Tatsumi, High-Performance Titanosilicate Catalyst Obtained through Combination of Liquid-Phase and Solid-Phase Transformation Mechanisms, *Chemcatchem*, 2014, **6**, 2719-2726.

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