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Supplementary Information

Intermediate-Crystallization Promoted Catalytic Activity of Titanosilicate Zeolites

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Table of Contents

1. Experimental section
2. Characterizations
3. Catalytic tests
4. Supplementary Figures and Tables
5. References

Experimental section

Reactant agents.

All reagents were used as purchased commercially without any further purification. Tetraethylorthosilicate (TEOS, Tianjin Fuchen Chemical Reagent Factory), tetrapropylammonium hydroxide (TPAOH) (40% Alfa), tetrabutyl titanate (TBOT) (98%, Guangfu Fine Chemical Research Institute), tert-butyl hydroperoxide (TBHP) (65%, Sinopharm Chemical Reagent Co.). Ceric Sulfate and 1-octane was purchased from Beijing Chemical Works. Ferroin indicator, dibenzothiophene (DBT) (98%) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) (99%) were purchased from Energy Chemical Co.

Dealuminated zeolite Beta Seeds.

Aluminosilicate Beta zeolite seeds were purchased from Alfa Company. The zeolite was dealuminated by refluxing in 13 mol/L HNO_3 (20 mL/g zeolite) for 24h. And washed thoroughly with deionized water until the pH value of the filtrate was neutral, and then dried at 100 °C in the oven overnight.

Synthesis of nano-sized Ti-Beta zeolites (Ti-Beta-3d and Ti-Beta-6d).

To obtain the pure titanosilicate ***BEA** here, we used the dealuminated zeolite Beta as the zeolite seeds. The nano-sized Ti-Beta zeolites were synthesized with the molar composition of 1.0 SiO_2: 0.025 TiO_2: 0.55 TEAOH: 5 H_2O: 10 wt% Seeds, under hydrothermal conditions at 150 °C with the crystallization time of 3 or 6 days, and the resulting products were named as Ti-Beta-3d and Ti-Beta-6d. Typically, the initial gel was prepared by mixing the TEAOH with distilled water, followed by the addition of TEOS and TBOT, and then stirred for 2 h continuously. Finally, the dealuminated zeolite Beta seeds were added into the solution and stirred for another 2 h continuously. The resulting mixture was charged into autoclaves and crystallized in a conventional oven at 150 °C. The as-synthesized solid products were washed thoroughly with water and ethanol, and then dried at 80 °C in the oven overnight, followed by calcination in air atmosphere at 550 °C for 6 h.

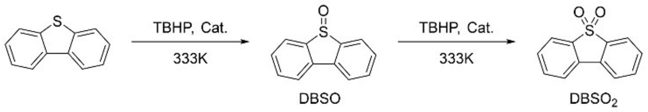
Material Characterization

Powder X-ray diffraction analysis of the samples was carried out on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å, 50 KV). The scanning electron microscope (SEM) images were obtained with a JSM-6700F electron microscope. Transmission electron microscopy (TEM) images were recorded on JEM-2200FS and JEM-2100 electron microscope. Nitrogen adsorption-desorption measurements were carried out on a

Micromeritics ASAP 2020 Plus analyzer at 77 K. Before starting the N_2 adsorption measurements, all the samples were activated by degassing in-situ at about 573 K for 10 h. Chemical compositions were determined with Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) analysis performed on an iCAP 7000 SERIES. Infrared spectra (IR) were recorded by Nicolet Impact 410 FTIR Infrared Instrument using KBr pellet technique. The Ultraviolet Visible diffuse reflectance spectroscopy (UV-Vis DRS) of the catalysts was recorded over the range of 190 nm to 500 nm against the support as reference, on a SHIMADZU U-4100. Ultraviolet Raman resonance spectroscopy (UV-Raman) (320 nm) were recorded on a DL-2 Raman spectrometer using the 320 nm line of a He–Ge laser as the excitation source and a Princeton CCD as the detector. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 X-ray photoelectron spectrometer using Al as the exciting source. The spectral resolution was 4 cm^{-1} and the laser power at the sample was less than 5 mW. ^{29}Si MAS NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer at resonance frequencies of 100.6 MHz with a spinning rate of 8 KHz. Chemical shifts of ^{29}Si is referenced to 2,2-dimethyl-2-ilapentane-5-sulfonate sodium salt (DSS).

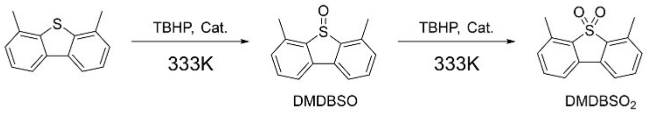
Catalytic tests

The oxidation of dibenzothiophene (DBT):



A certain amount of DBT was dissolved in n-octane to act as model fuel, and the concentration of sulfur in the model fuel was about 500 ppm. The reaction was performed in a 50 mL three neck glass flask with an oil bath under vigorous stirring (600 rap/min). In a standard run, 10 mL of model fuel and proper amount of catalyst were added to the reactor, with the mole of reactant to titanium in zeolite catalysts fixed at 10. Tert-butylhydroperoxide (TBHP) was used as oxidant, and the molar ratio of TBHP/DBT was 2. The reaction was carried at 333 K for 30 min. Then, filtering the reacted solution and analyzing the TBHP conversion by titration with $Ce(SO_4)_2$ and Ferroin indicator. The products were analyzed by Gas chromatography-mass spectrometry (GC-MS, Thermo Fisher Trace ISQ, equipped with TG-5MS column, 60 m × 320 µm × 25 µm). Mass balances were accurate within 5%.

The oxidation of 4,6-dibenzothiophene (4,6-DMDBT):



A certain amount of 4,6-DMDBT was dissolved in n-octane to act as model fuel, and the concentration of sulfur in the model fuel was about 500 ppm. The reaction was performed in a 50 mL three neck glass flask with an oil bath under vigorous stirring (600 rap/min). In a standard run, 10 mL of model fuel and proper amount of catalyst were added to the reactor, with the mole of reactant to titanium in zeolite catalysts fixed at 10. TBHP was used as oxidant, and the molar ratio of TBHP/4,6-DMDBT was 2. The reaction was carried at 333 K for 30 min. Then, filtering the reacted solution and analyzing the TBHP conversion by titration with $Ce(SO_4)_2$ and Ferroin indicator. The products were analyzed by Gas chromatography-mass spectrometry (GC-MS, Thermo Fisher Trace ISQ, equipped with TG-5MS column, 60 m × 320 µm × 25 µm). Mass balances were accurate within 5%.

The sulfides removal rate was expressed as:

$$\text{Sulfur removal rate} = \frac{\text{C(sulphide)}_{\text{initial}} - \text{C(sulphide)}_{\text{sample}}}{\text{C(sulphide)}_{\text{initial}}}$$

where $\text{C(sulphide)}_{\text{initial}}$ and $\text{C(sulphide)}_{\text{sample}}$ were the initial and residual sulfur contents of the model oil, respectively.

TON of the oxidation of sulphides was calculated as follows:

$$\text{TON} = \frac{\left(\text{n}\left(\text{sulphide}\right)_{\text{initial}} - \text{n}\left(\text{sulphide}\right)_{\text{sample}}\right) + n(sulphone)_{sample}}{\text{n(Ti)}}$$

TOF of the oxidation of sulphides was calculated as follows:

$$\text{TOF} = \frac{\text{n(sulphide)}_{\text{initial}} - \text{n(sulphide)}_{\text{sample}}}{\text{n(Ti)} * Reaction\ Time}$$

Yield of the products was calculated with:

Yield (product) =Conversion (sulphide) × Selectivity (product)

Supplementary Figures and Tables

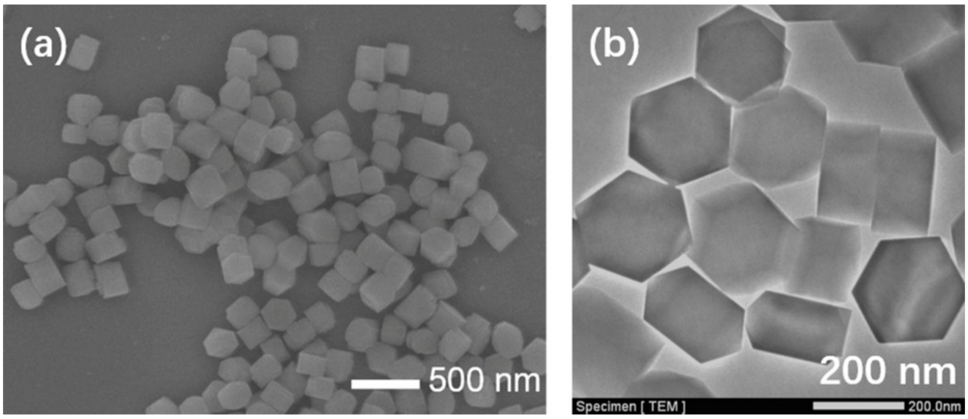


Figure S1. SEM image and TEM image of nano-sized silicalite-1 zeolite seeds for the synthesis of TS-1(H_x) zeolites.

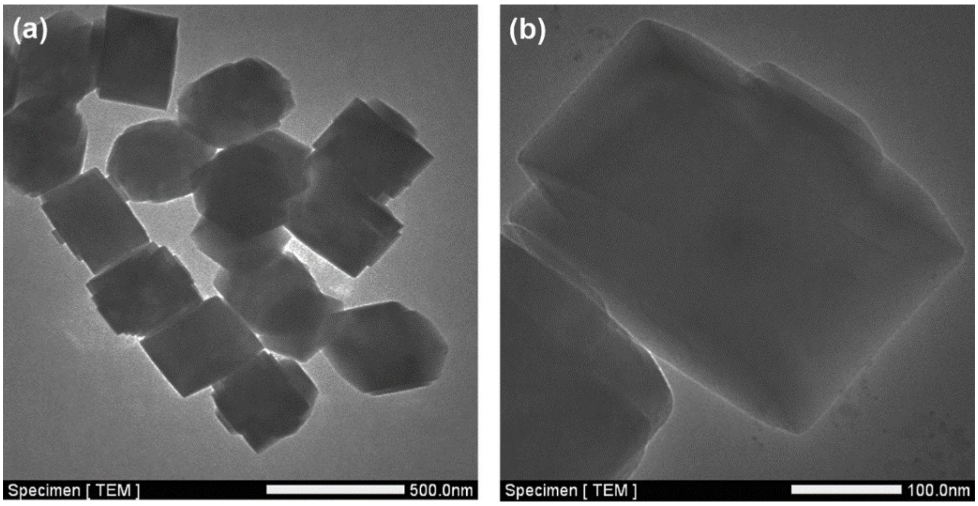


Figure S2. TEM images of the conventional nano-sized TS-1(con) zeolite.

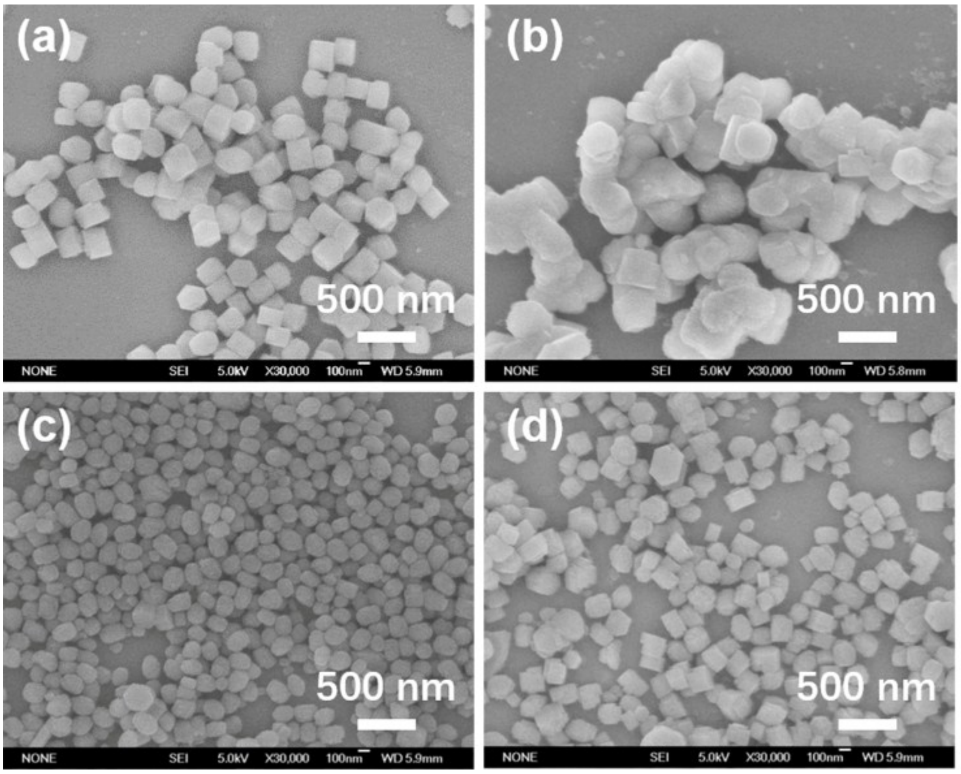


Figure S3. SEM images of nano-sized TS-1(con) (a), TS-1(H1) (b), TS-1(H3) (c), and TS-1(H24) (d) zeolite catalysts.

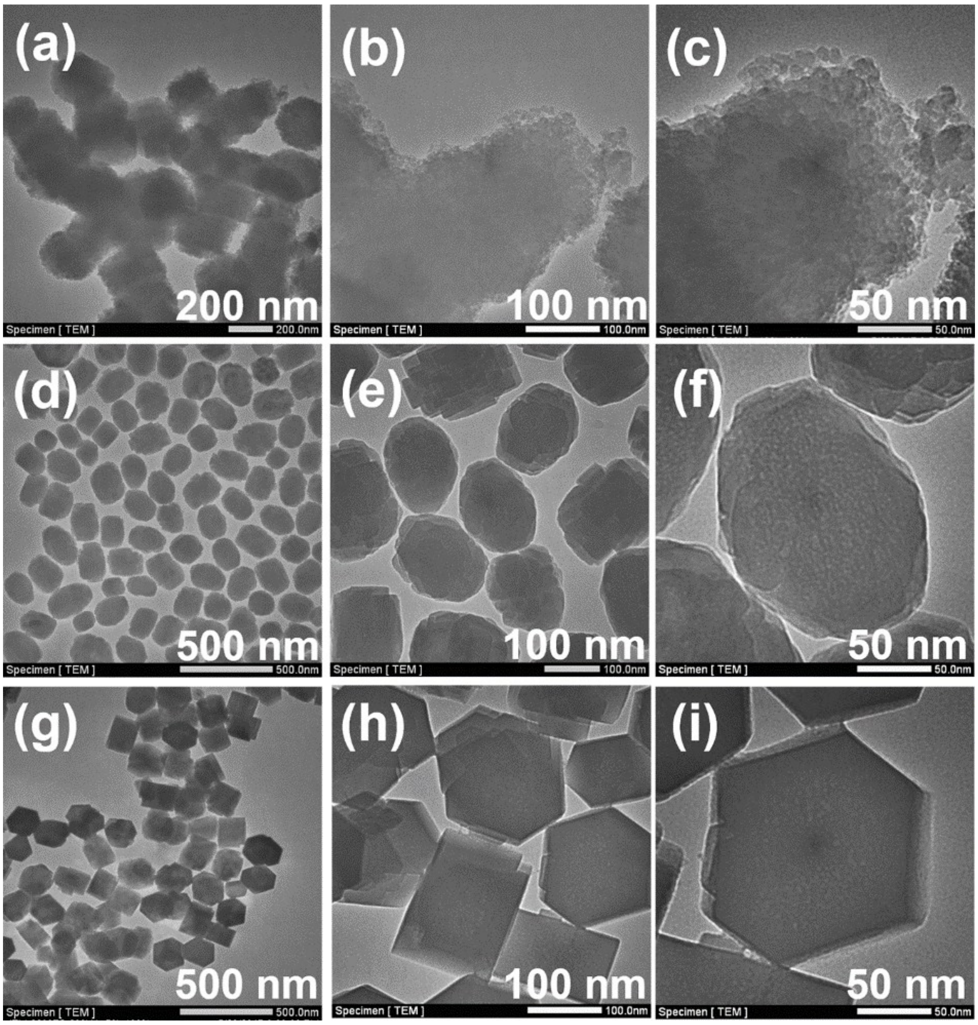


Figure S4. TEM images of nano-sized hierarchical TS-1(H1) (a-c), TS-1(H3) (d-f) and TS-1(H24) (g-i) zeolite catalysts.

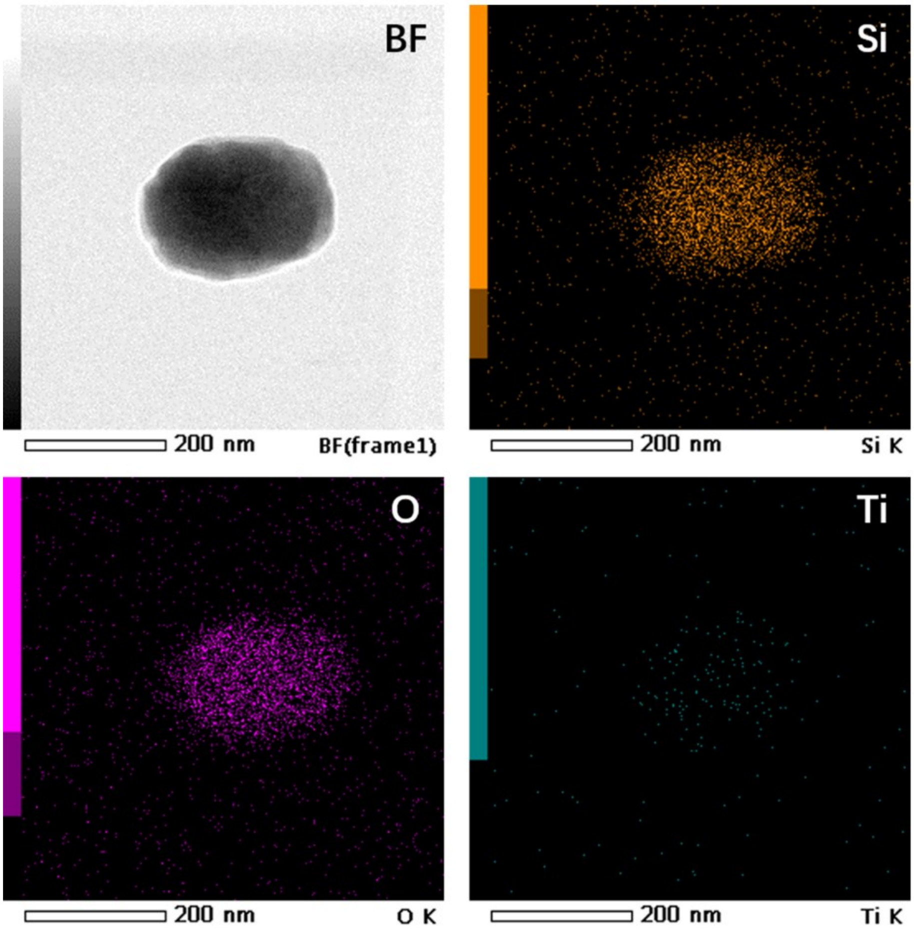


Figure S5. Bright field image and elemental mappings for Si, O and Ti elements of TS-1(H3) zeolite sample.

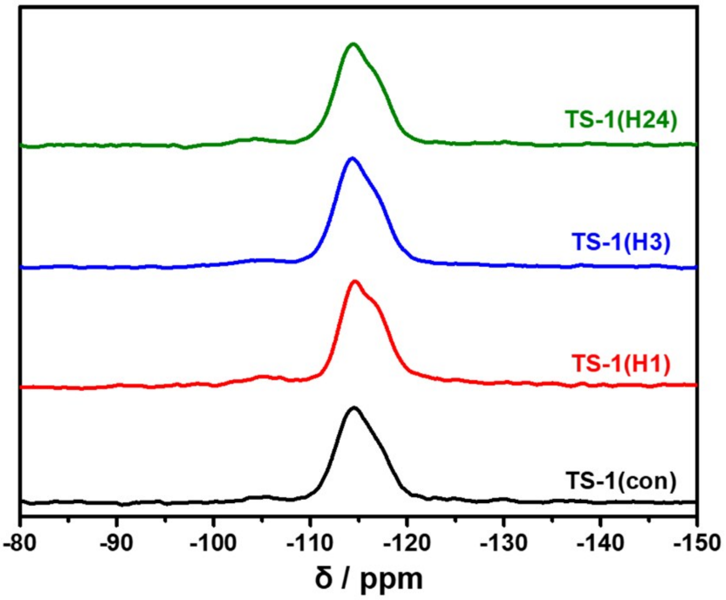


Figure S6. ^{29}Si MAS NMR spectra of nano-sized TS-1(con), TS-1(H1), TS-1(H3), and TS-1(H24) zeolite catalysts.

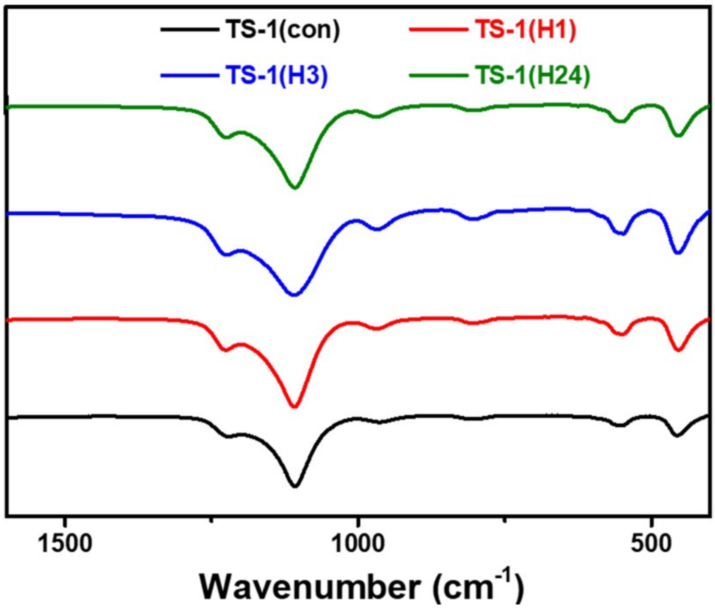


Figure S7. FT-IR spectra of nano-sized TS-1(con), TS-1(H1), TS-1(H3), and TS-1(H24) zeolite catalysts.

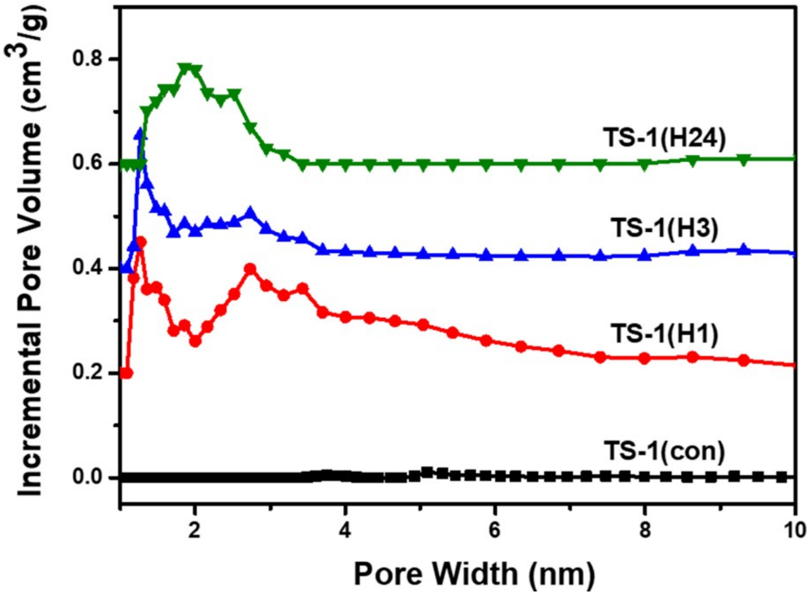


Figure S8. Pore size distributions of nano-sized TS-1(con), TS-1(H1), TS-1(H3), and TS-1(H24) zeolite catalysts.

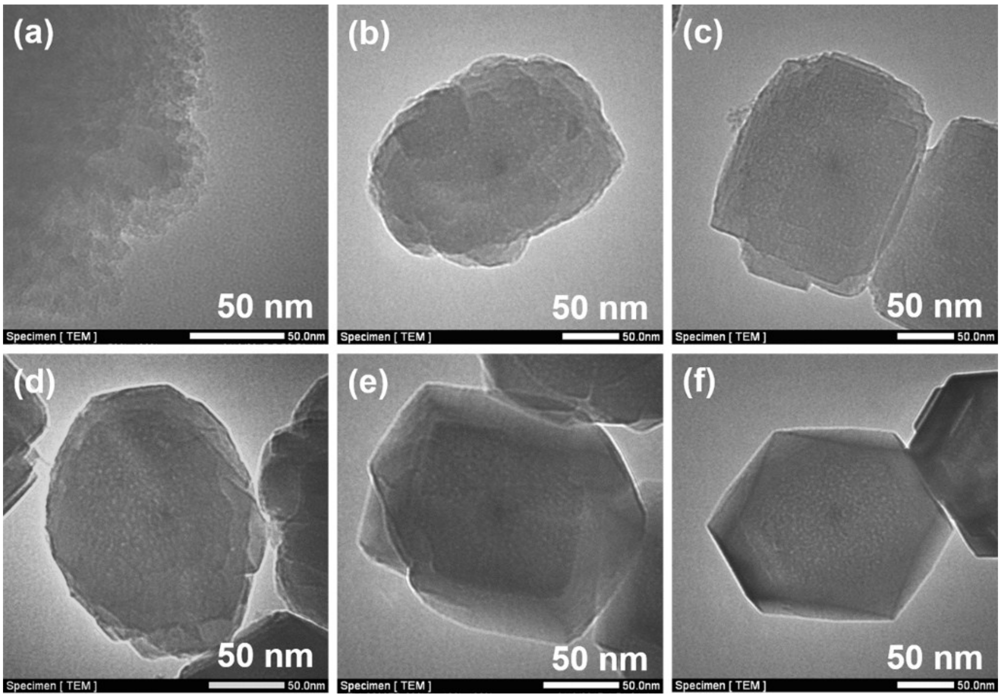


Figure S9. TEM images of TS-1(Hx) catalysts, synthesized at different crystallization times (a)1 h, (b) 2 h, (c) 3 h, (d) 6 h, (e) 12 h, and (f) 24 h.

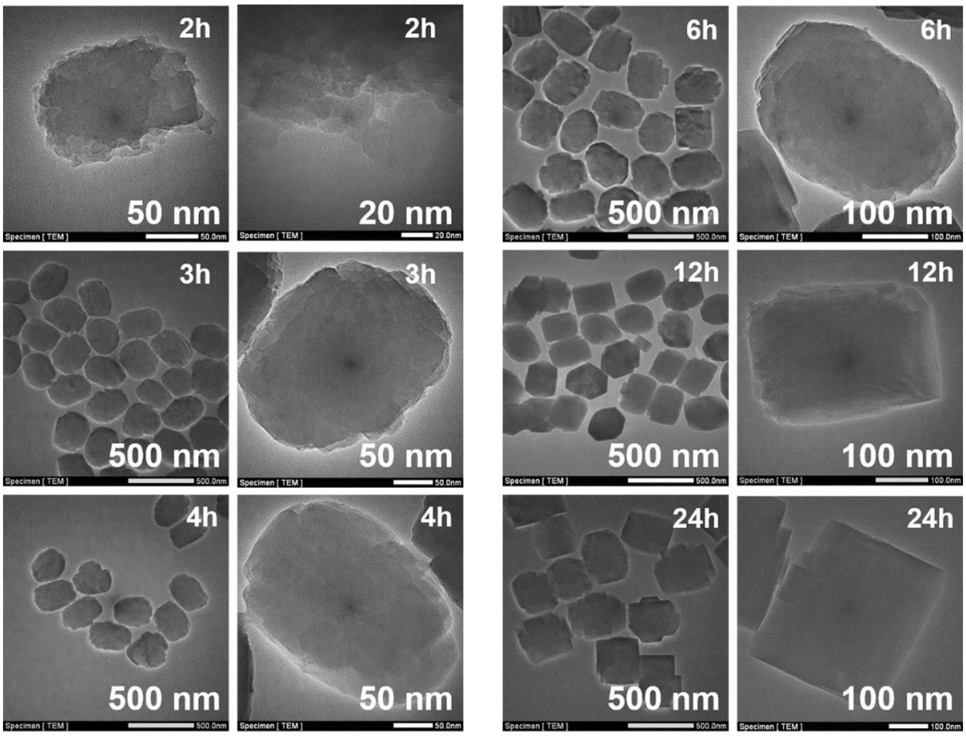


Figure S10. TEM images of the conventional nano-sized TS-1(Cx) zeolite samples without adding zeolite seeds synthesized at different crystallization times from 2 to 24 h.

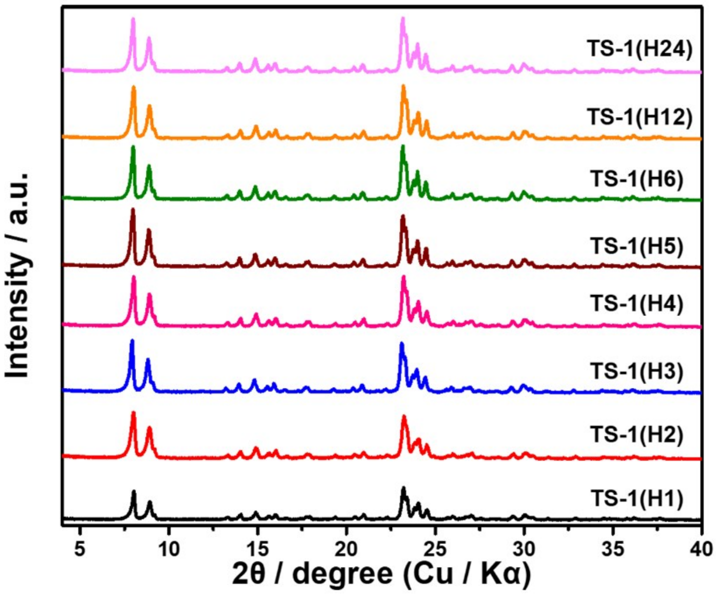


Figure S11. XRD patterns of seed-assisted nano-sized hierarchical TS-1(Hx) zeolite samples crystallized at different times ranging from 1 to 24 h.

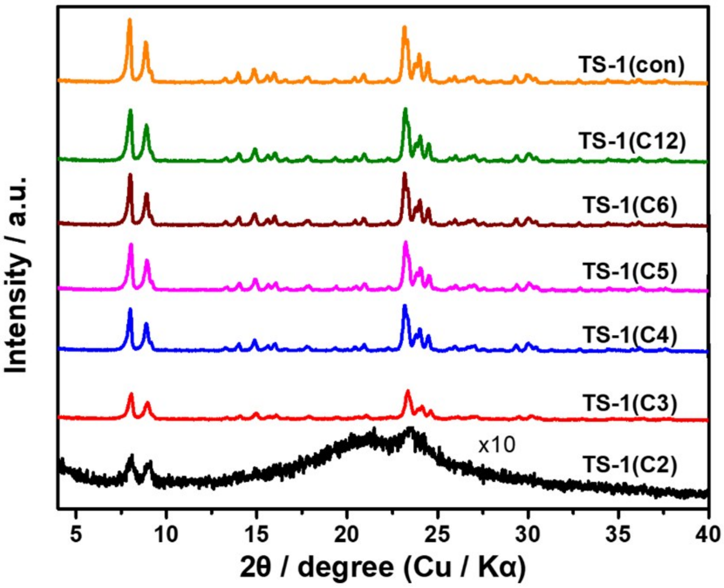


Figure S12. XRD patterns of conventional nano-sized TS-1(Cx) zeolite samples crystallized at different times ranging from 2 to 24 h.

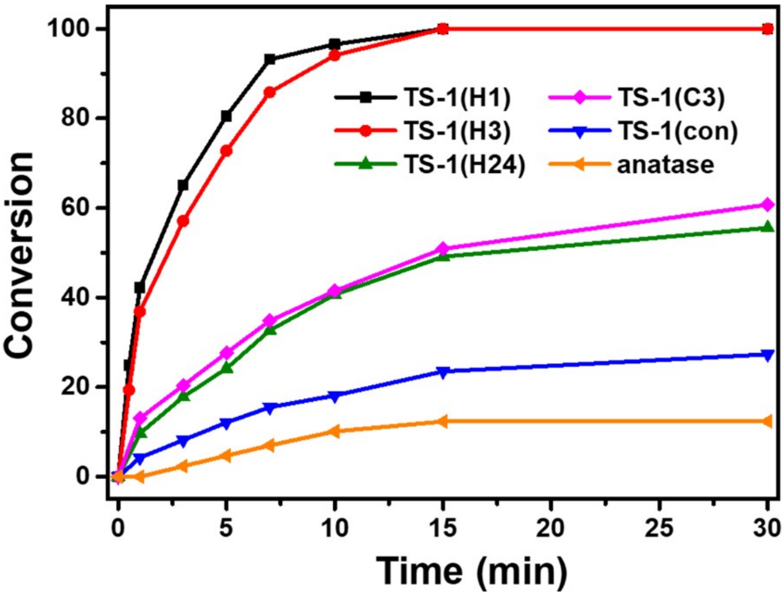


Figure S13. Catalytic oxidation of DBT with TBHP over intermediately and completely crystallized TS-1(H1), TS-1(H3), TS-1(H24), TS-1(C3) and TS-1(con) zeolite catalysts as well as the anatase. Reaction conditions: 10mL 500ppm model fuels, 60 °C, the molar ratio of n(DBT)/n(Ti in zeolite) was fixed at 10, n(DBT)/n(TBHP) was 0.5.

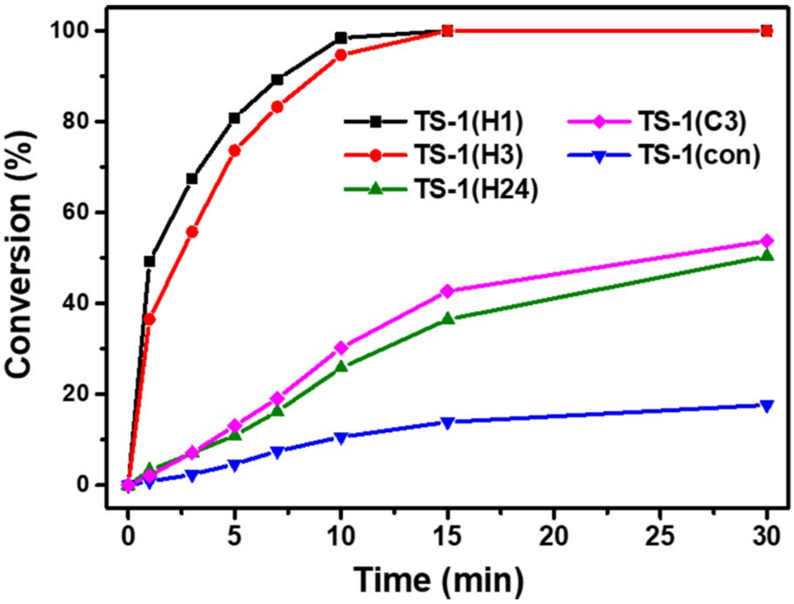


Figure S14. Catalytic oxidation of 4,6-DMDBT with TBHP over intermediately and completely crystallized TS-1(H1), TS-1(H3), TS-1(H24), TS-1(C3) and TS-1(con) zeolite catalysts. Reaction conditions: 10mL 500ppm model fuels, 60 °C, the molar ratio of n(4,6-DMDBT)/n(Ti in zeolite) was fixed at 10, n(4,6-DMDBT)/n(TBHP) was 0.5.

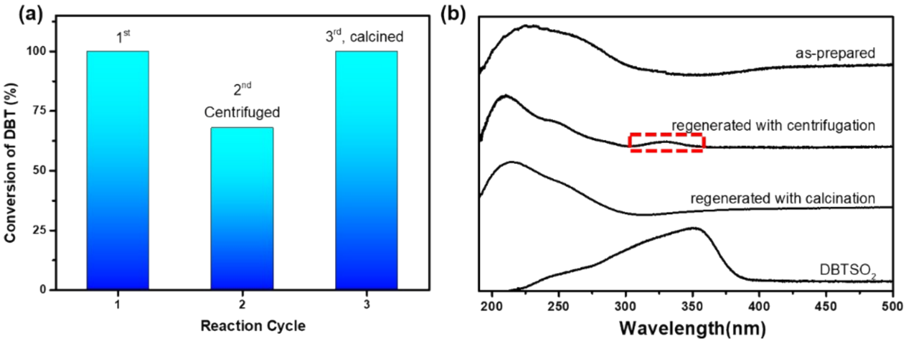


Figure. S15. Catalytic activity of oxidation of DBT (a) and UV-vis spectroscopy (b) of the fresh, used and regenerated catalysts. Reaction condition: 10 mL 500 ppm DBT model fuels, 60 °C, 15 min, the molar ratio of n(4,6-DMDBT)/n(Ti in zeolite) was fixed at 10, n(4,6-DMDBT)/n(TBHP) was 0.5.

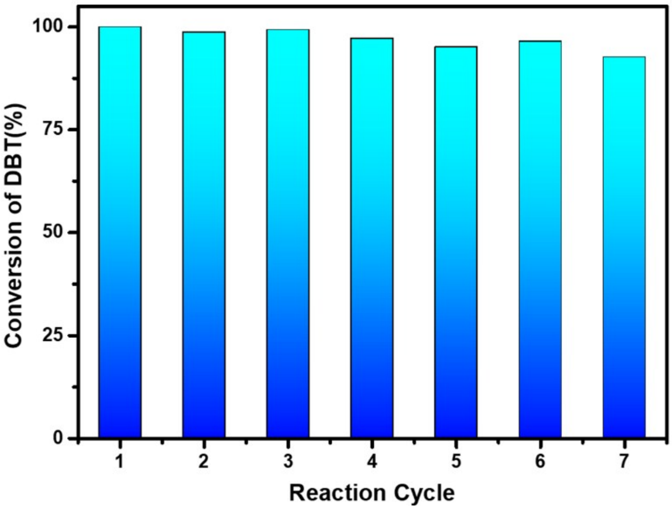


Figure S16. Recycle tests in the oxidation of DBT over TS-1(H3) catalyst. Reaction condition: 10 mL 500 ppm DBT model fuels, 60 °C, 15 min, the molar ratio of n(4,6-DMDBT)/n(Ti in zeolite) was fixed at 10, n(4,6-DMDBT)/n(TBHP) was 0.5.

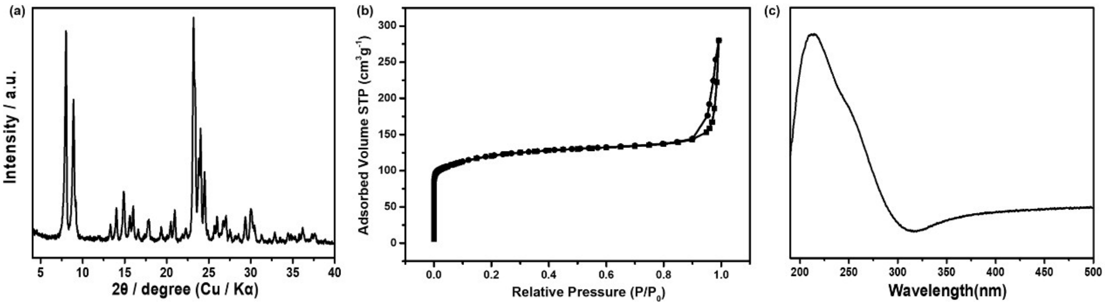


Figure S17. XRD pattern (a), N_2 adsorption-desorption isotherm (b), and UV-vis spectrum (c) of the TS-1(H3) sample after seven cycles in the oxidation of DBT.

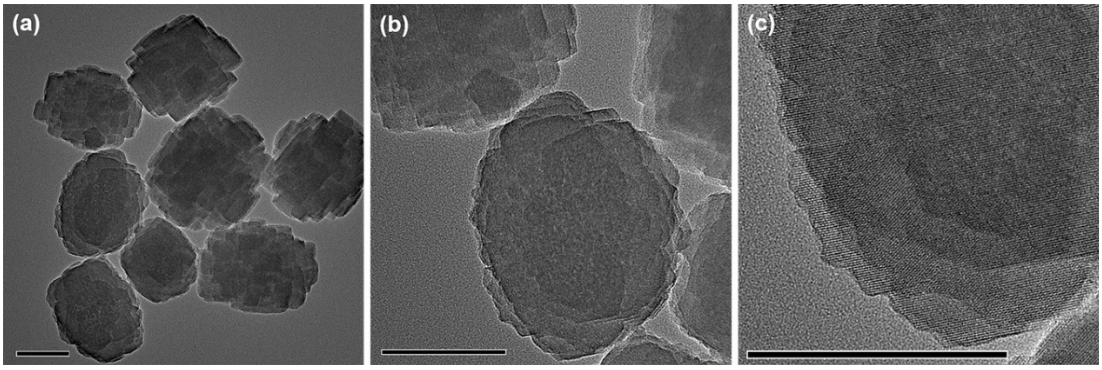


Figure S18. Low-magnification (a) and high-magnification (b, c) TEM images of the TS-1(H3) sample after seven cycles in the oxidation of DBT. Scale bar, 100nm.

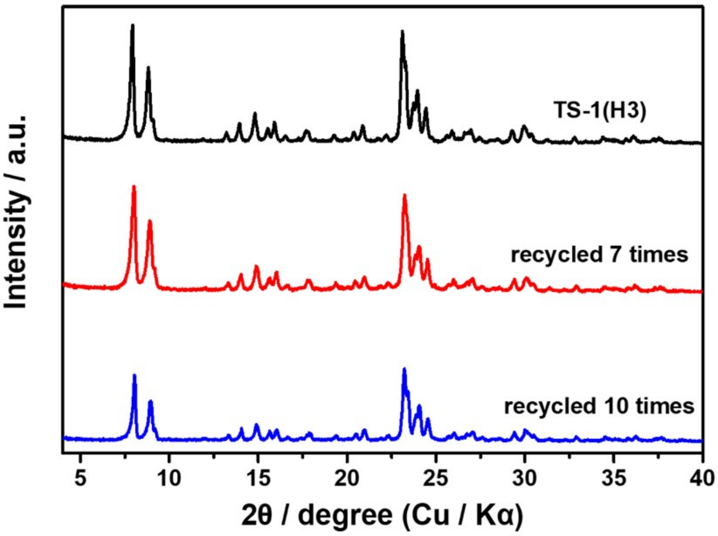


Figure S19. XRD patterns of the fresh and recycled TS-1(H3) sample.

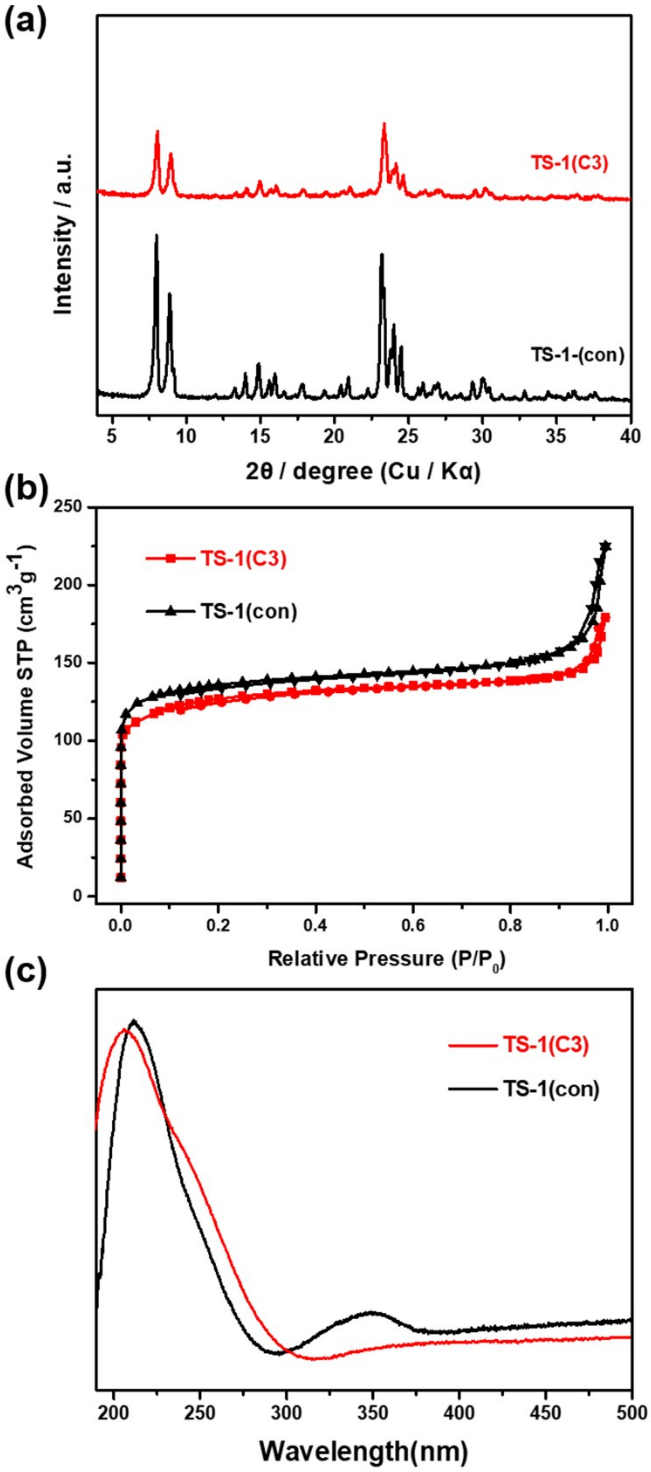


Figure S20. XRD patterns (a), N_2 adsorption and desorption isotherms (b), and UV-Vis spectra (c) of the intermediately crystallized conventional TS-1(C3) and the completely crystallized conventional TS-1(con) zeolite catalysts.

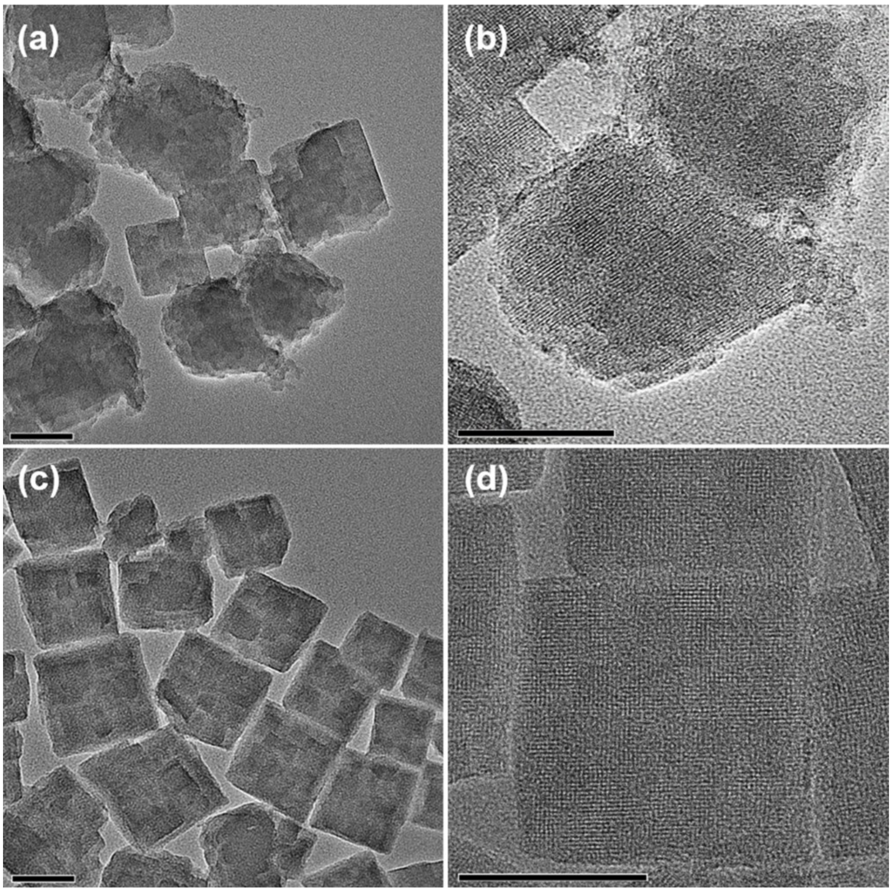


Figure S21. TEM images of nano-sized Ti-Beta-3d (a, b) and Ti-Beta-6d (c, d) zeolite catalysts. Scale bar, 50nm.

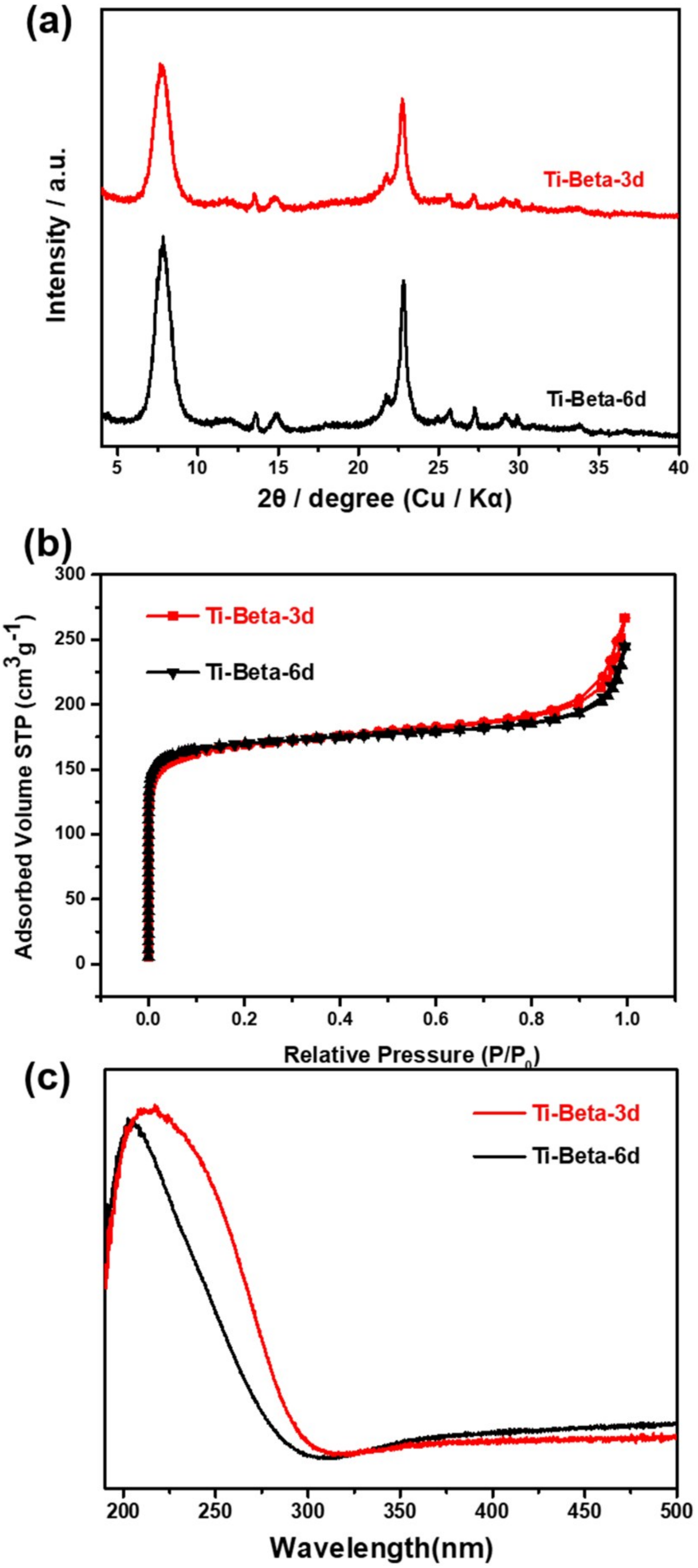


Figure S22. XRD patterns (a), N_2 adsorption and desorption isotherms (b), and UV-Vis spectra (c) of the intermediately crystallized nano-sized Ti-Beta-3d and the completely crystallized nano-sized Ti-Beta-6d zeolite catalysts.

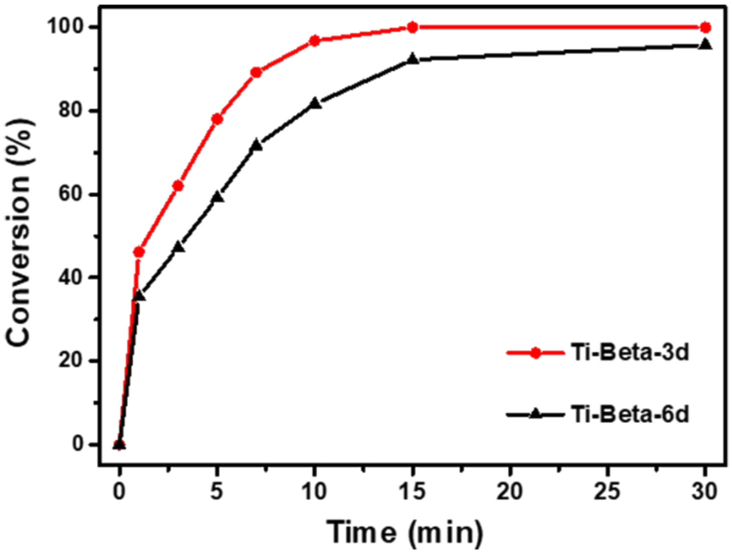


Figure S23. Catalytic oxidation of DBT with TBHP over intermediately crystallized Ti-Beta-3d and completely crystallized Ti-Beta-6d zeolite catalysts. Reaction conditions: 10mL 500ppm model fuels, 60 °C, the molar ratio of n(DBT)/n(Ti in zeolite) was fixed at 10, n(DBT)/n(TBHP) was 0.5.

Table S1. Framework composition, porous porosity and product yield of the prepared zeolite catalysts.

Samples	Si/Ti[a]	S_{BET}[b] (m^2/g)	S_{micro}[c] (m^2/g)	S_{ext}[c] (m^2/g)	V_{micro}[c] (cm^3/g)	V_{total}[d] (cm^3/g)	V_{meso}[e] (cm^3/g)	Yield[f] (%)
TS-1(H1)	160.5	464	249	215	0.12	0.31	0.19	8.4
TS-1(H3)	83.6	426	277	149	0.13	0.36	0.23	75.9
TS-1(H3)-7[g]	90.3	398	264	134	0.13	0.30	0.17	-
TS-1(H3)-10[h]	97.1	-	-	-	-	-	-	-
TS-1(H24)	77.8	413	295	118	0.14	0.32	0.18	96.3
TS-1(C3)	97.3	422	296	126	0.14	0.25	0.11	67.8
TS-1(con)	73.2	450	345	105	0.14	0.25	0.11	96.3
Ti-Beta-3d	60.2	617	400	217	0.16	0.56	0.40	-
Ti-Beta-6d	39.4	628	523	105	0.25	0.60	0.35	-

[a] Measured by inductively coupled plasma (ICP). [b] Specific surface area calculated from the nitrogen adsorption isotherm using the BET method. [c] S_{micro} (micropore area), S_{ext} (external surface area), and V_{micro} (micropore volume) calculated using the t-plot method. [d] Total pore volume at $P/P_0 = 0.995$. [e] $V_{meso} = V_{total} – V_{micro}$. [f] Yield = (w1-w2)/w3*100%, where w1, w2, and w3 are the weight of the calcined sample, seeds and theoretical TS-1 sample, respectively. [g] The catalyst was used after 10-reaction-regeneration cycle times. [h] The catalyst was used after 10 reaction-regeneration cycle times.

Table S2. Relative crystallinity and yield of nano-sized hierarchical TS-1(Hx) samples with different crystallization time.

	Intensity of Peaks[a]			Yield	Relative
	23.1°	24.0°	24.5°	(%)[b]	Crystallinity (%)[c]
TS-1(H1)	6938	3502	2214	8.4	57.0
TS-1(H2)	9577	4310	3316	67.4	77.4
TS-1(H3)	9929	4978	3404	75.9	82.4
TS-1(H4)	10750	5630	3488	83.4	89.4
TS-1(H5)	11098	5776	3891	83.8	93.5
TS-1(H6)	11319	6155	3800	86.3	95.8
TS-1(H12)	11675	5926	4089	90.4	97.6
TS-1(H24)	11919	6310	3986	96.3	100.0

[a] Based on the XRD patterns of samples in Figure S11. [b] Yield = (w1-w2)/w3*100%, where w1, w2, and w3 are the weight of the calcined sample, seed and theoretical TS-1 sample, respectively. [c] The relative crystallinity is calculated based on the intensity of the three peaks (2θ=23.1°, 24.0°, and 24.5°) in the XRD patterns, with the equation: $\text{Crystallinity}=\sum I/\sum I_r \times 100\%$, where I is the line intensity of the sample and I_r is the line intensity of the reference sample (with the highest crystallinity).[S1]

Table S3. Relative crystallinity and yield of conventional nano-sized TS-1(Cx) samples with different crystallization time.

	Intensity of Peaks[a]			Yield	Relative
	23.1°	24.0°	24.5°	(%)[b]	Crystallinity (%)[c]
TS-1(C2)	1554	1329	1499	27.0	20.8
TS-1(C3)	5938	2828	1938	67.8	50.7
TS-1(C4)	9117	4572	3173	75.5	79.9
TS-1(C5)	9707	4638	3155	78.2	82.9
TS-1(C6)	10421	5262	3497	82.5	90.9
TS-1(C12)	10489	5070	3721	89.8	91.3
TS-1(con)	11106	5853	4149	96.3	100

[a] Based on the XRD patterns of samples in Figure S12. [b] Yield = w1/w2*100%, where w1 and w2 are the weight of the calcined sample and theoretical TS-1 sample, respectively. [c] The relative crystallinity is calculated based on the intensity of the three peaks (2θ=23.1°, 24.0°, and 24.5°) in the XRD patterns, with the equation: Crystallinity=$\sum I/\sum I_r \times 100\%$, where I is the line intensity of the sample and I_r is the line intensity of the reference sample (with the highest crystallinity).[S1]

Table S4 Comparison of catalytic performance over some representative hierarchical TS-1 catalysts in oxidation desulfurization of DBT

Catalyst	Ti / wt%	Mass of catalyst / mg	S content / ppm	Oxidant	Oxidant / S	Temp. / K	Reaction Time/min	Removal of DBT/%	TOF / h^{-1}	Ref.
TS-1(H3)	0.94[a]	55	500	TBHP	2	333	15	100	232.2[b, c] 40.0[d]	This work
HTS-1B	3.40[a]	50	500	TBHP	2	333	240	100	0.8[d]	S2
HTS-1C	2.11[a]	50	500	TBHP	2	333	180	100	1.7[d]	S3
Hierarchical TS-1C	2.00[a]	50	500	TBHP	2	333	30	100	10.5[d]	S4
HTS-1-a	-	50	1000	TBHP	3	333	240	100	3.7[d, e]	S5
Ti-B-M-DA	5.5	50	1000	TBHP	6	333	20	100	58.8[d, e]	S6
Ti/MM-0.5	3.91	50	1000	H_2O_2	6	333	120	99	4.3[d, e]	S7
HTS-1b	2.02	50	1000	TBHP	4	333	60	100	114.9[c, e] 14.8[d]	S8

[a] Ti content was calculated according to Si/Ti ratio. [b] TOF is calculated when the conversion of DBT below 20%. [c] Initial TOF Value. [d] TOF is calculated when the conversion of DBT reaches 100% according to the reported data (overall TOF Value). [e] from the references.

Table S5. Relative crystallinity of fresh and recycled TS-1(H3) sample

	Intensity of Peaks[a]			Relative
	23.1°	24.0°	24.5°	Crystallinity (%)[b]
TS-1(H3)	9929	4978	3404	100
TS-1(H3)-7[c]	9356	4475	3245	93.2
TS-1(H3)-10[d]	7036	3513	2377	70.6

[a] Based on the XRD patterns of samples in Figure S19. [b] The relative crystallinity is calculated based on the intensity of the three peaks (2θ=23.1°, 24.0°, and 24.5°) in the XRD patterns, with the equation: $\text{Crystallinity}=\sum I/\sum I_r \times 100\%$, where I is the line intensity of the sample and I_r is the line intensity of the reference sample (with the highest crystallinity).[S1] [c] After seven reaction-regeneration cycles. [d] After ten reaction-regeneration cycles.

Table S6. Oxidative desulfurization of DBT with TBHP over Ti-Beta Catalysts.

Samples	Conv. (%)[a]		TON[b]	Yield (%)[c]	
	DBT	TBHP		DBSO	$DBSO_2$
Ti-Beta-3d	100	90.3	16.1	38.5	61.5
Ti-Beta-6d	96.2	85.8	13.9	53.1	43.1

[a] Calculated after 30 min of the reaction. [b] Turnover number (moles of converted DBT+$DBSO_2$ per mole of Ti site). [c] Product yield based on DBT after 30 min of the reaction.

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