

***In-situ* structural reconstruction triggers the hydrothermal synthesis
of hierarchical Ti-Beta zeolites for oxidative desulfurization**

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Table S1 Oxidative desulfurization of dibenzothiophene in fuel oil over various zeolite-based catalytic systems.

No.	Catalyst	O/S	Time (h)	Removal (%)	CE ^a (h ⁻¹ mol ⁻¹)	Ref.
1	W-MFI	3	2	20.0	580.2	1
2	V-impregnated ZSM-5	14	2	79.3	1428.0	2
3	Mn-impregnated ZSM-5	14	2	18.5	362.7	2
4	Ti-MWW	4	3	95.0	1916.7	3
5	TS-1	4	3	4.2	83.3	3
6	Ti-Beta	4	3	84.0	4375.0	4
7	Ti-MCM-41	4	3	94.0	5000.0	4
8	Ti-HMS	17	5	67.0	414.6	5
9	hierarchical Ti-MOR	6	2	99.0	3253.4	6
10	Ta-Beta	3	2	99.2	14319.4	7
11	hierarchical TS-1	2	2	95.0	10545.0	8
12	Ti-Beta-HT-0.5-50	3	0.5	98.3	56171.4	this work

^a Catalytic efficiency (CE), moles of dibenzothiophene sulfone formed hourly per mole of metal sites in catalyst per mole of H₂O₂.

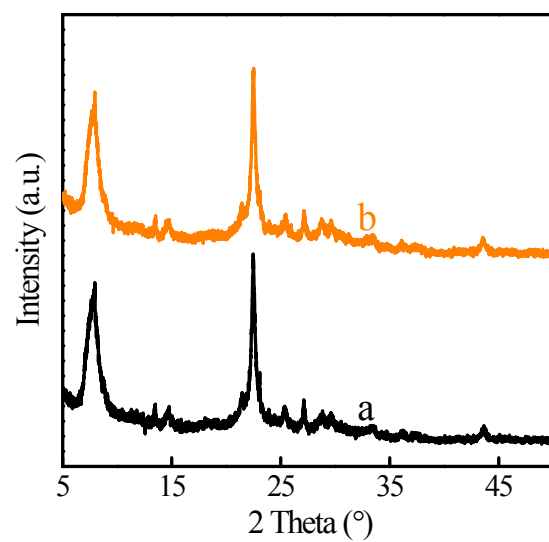


Fig. S1 XRD patterns of Al-Beta (a) and dealuminated Beta-DA (b) samples.

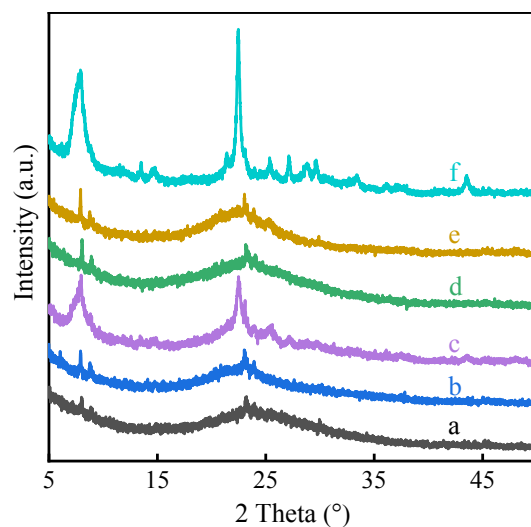


Fig. S2 XRD patterns of calcined solid products derived from different raw materials, Beta-DA and TEAOH (a); Beta-DA and NH_4F (b); Beta-DA and TBOT (c); Beta-DA, TBOT, and TEAOH (d); Beta-DA, TBOT, and NH_4F (e); Beta-DA, TBOT, TEAOH, and NH_4F (f). Crystallization conditions: TBOT if added, $\text{TiO}_2/\text{SiO}_2 = 0.02$; $\text{H}_2\text{O}/\text{SiO}_2 = 7.0$; TEAOH if added, $\text{TEAOH}/\text{SiO}_2 = 0.5$; NH_4F if added, $\text{NH}_4\text{F}/\text{SiO}_2 = 0.5$; temp., 140 °C; time, 1 d.

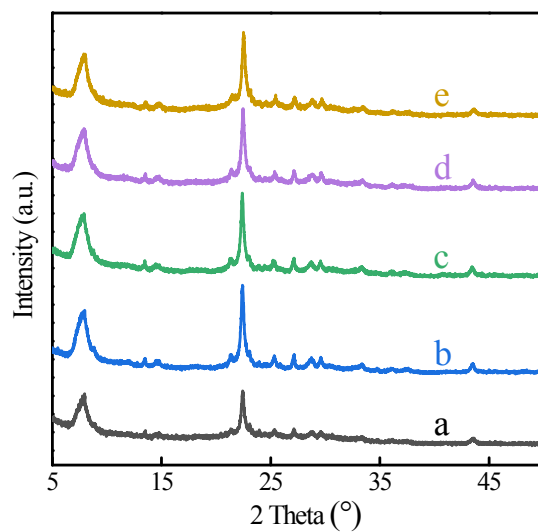


Fig. S3 XRD patterns of calcined Ti-Beta-HT crystallized at TEAOH/SiO₂ molar ratio of 0.1 (a), 0.2 (b), 0.4 (c), 0.5 (d), and 0.7 (e). Other crystallization conditions: TiO₂/SiO₂ = 0.02; H₂O/SiO₂ = 7.0; NH₄F/SiO₂ = 0.5; temperature, 140 °C; time, 1 d.

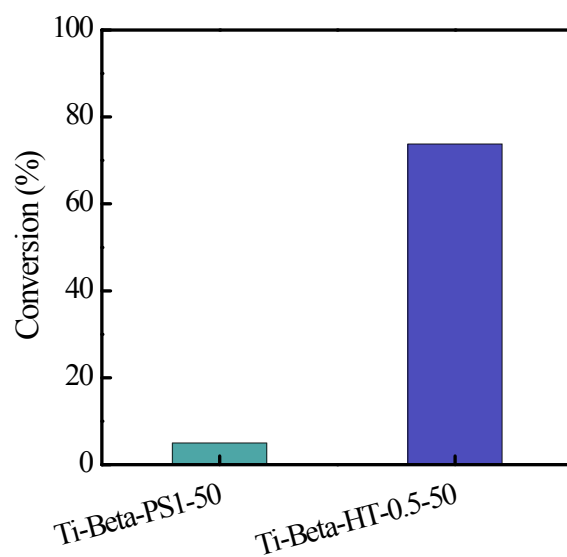


Fig. S4 The catalytic activities of TEAOH-NH₄F-free Ti-Beta-PS1-50 and Ti-Beta-HT-0.5-50 samples. Reaction conditions: catalyst, 35 mg; model oil (S content, 500 ppm), 10 mL; aqueous TBHP (70 wt%), 40 μ L, TBHP/DBT = 2; temp., 60 $^{\circ}$ C; time, 30 min.

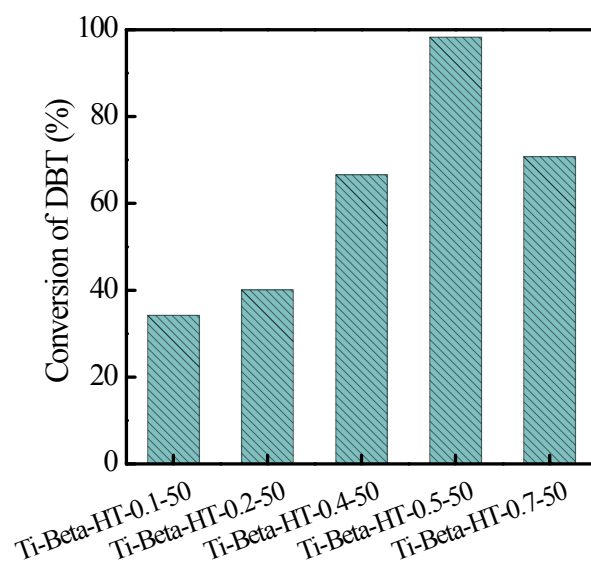


Fig. S5 The dependence of DBT conversion on TEAOH amounts used in the hydrothermal process. Reaction conditions: catalyst, 35 mg; model oil (S content, 500 ppm), 10 mL; aqueous TBHP (70 wt%), 60 μ L, TBHP/DBT = 3; temp., 60 $^{\circ}$ C; time, 30 min.

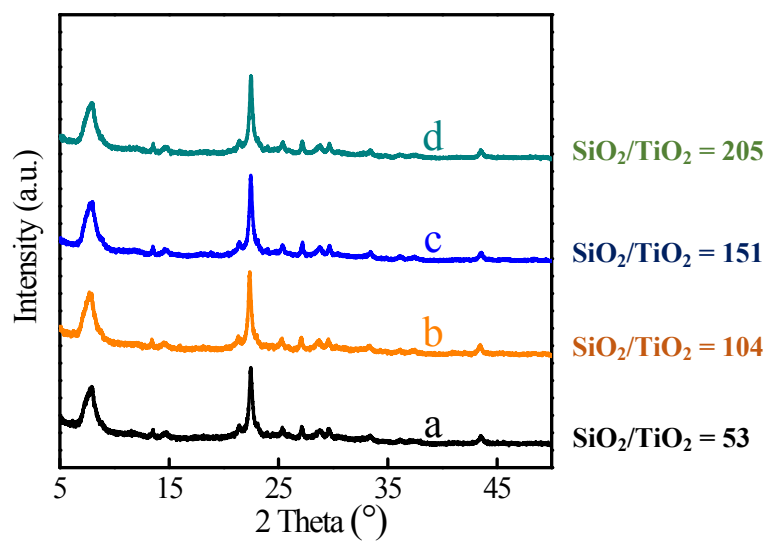


Fig. S6 XRD patterns and $\text{SiO}_2/\text{TiO}_2$ molar ratio of calcined Ti-Beta-HT product crystallized at $\text{SiO}_2/\text{TiO}_2$ molar ratio of 50 (a), 100 (b), 150 (c), and 200 (d) in the synthesis gels. Other crystallization conditions: $\text{TEAOH}/\text{SiO}_2 = 0.5$; $\text{H}_2\text{O}/\text{SiO}_2 = 7.0$; $\text{NH}_4\text{F}/\text{SiO}_2 = 0.5$; temperature, 140°C ; time, 1 d.

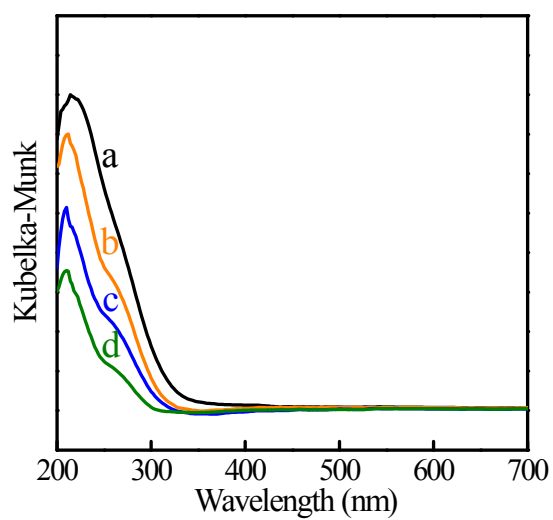


Fig. S7 UV-vis spectra of calcined Ti-Beta-HT crystallized at SiO₂/TiO₂ molar ratio of 50 (a), 100 (b), 150 (c), and 200 (d).

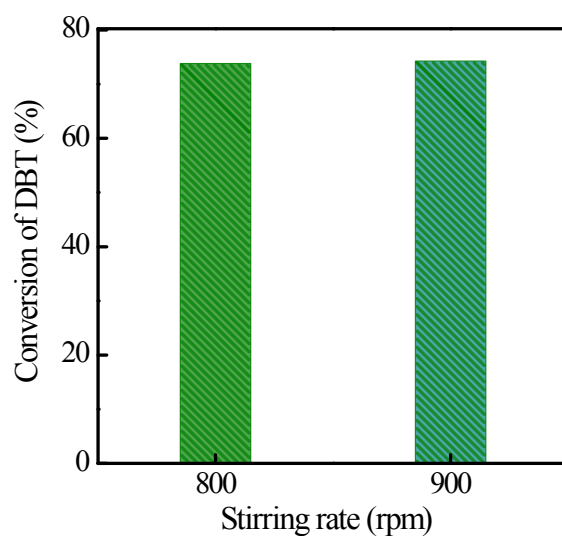


Fig. S8 The effect of stirring rate on the DBT oxidation. Reaction conditions: Ti-Beta-HT-0.5-50, 35 mg; model oil (S content, 500 $\mu\text{g mL}^{-1}$), 10 mL; aqueous TBHP (70 wt%), 40 μL , TBHP/DBT = 2; temp., 60 $^{\circ}\text{C}$; time, 30 min.

As shown in Fig. S8, DBT conversion was nearly not changed with the increase of stirring rate from 800 to 900 rpm, suggesting that external diffusion did not exist in this systems.⁹

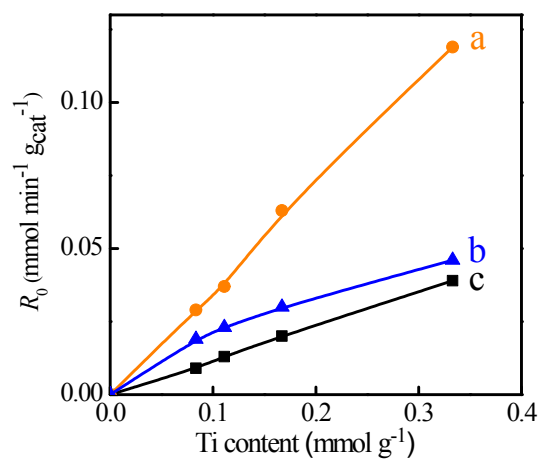


Fig. S9 The dependence of initial reaction rate (R_0) for DBT (a), 4,6-DMDBT (b), and BT (c) for on Ti content within Ti-Beta-PS zeolites. Reaction conditions: catalyst, 35 mg; model oil (S content, 500 ppm), 10 mL; aqueous TBHP (70 wt%), 40 μ L, TBHP/S = 2; temperature, 60 $^{\circ}$ C.

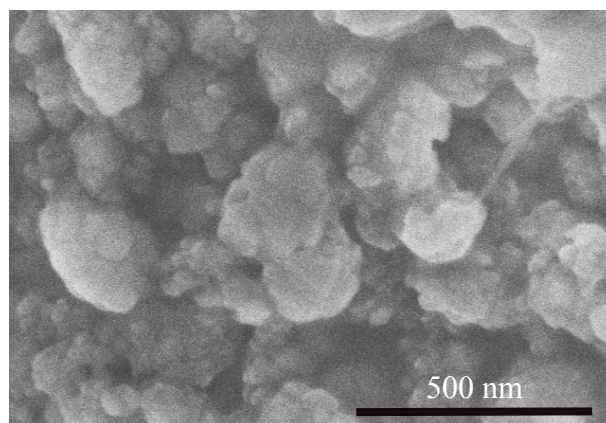


Fig. S10 SEM image of Ti-Beta-HT-0.5-100 sample.

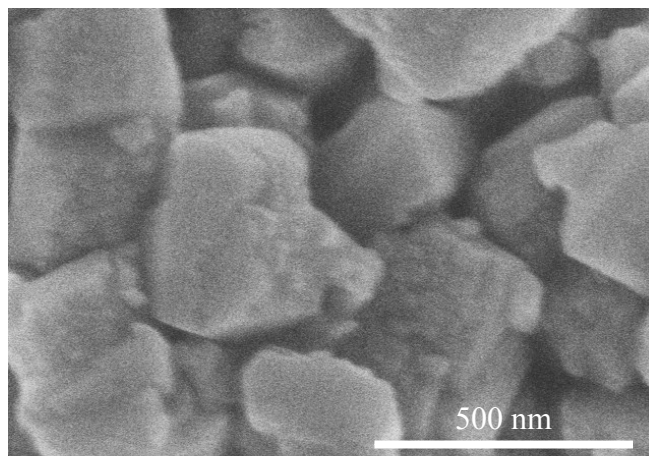


Fig. S11 SEM image of Ti-Beta-F-100 sample.

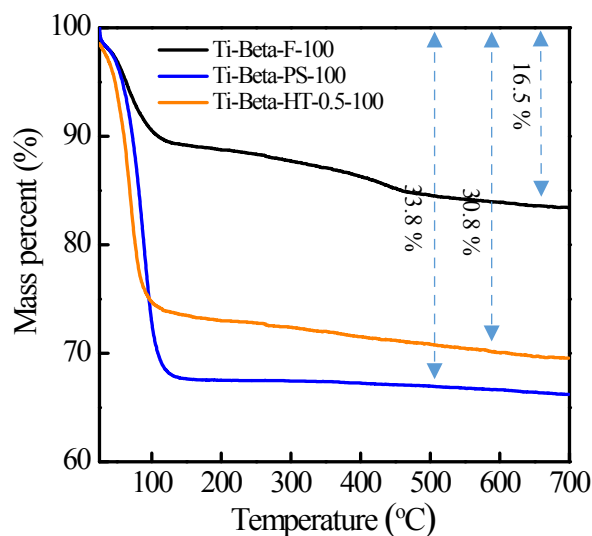


Fig. S12 TG curves of three Ti-Beta samples saturated with water vapor.

TG measurement was employed to investigate the hydrophilicity/hydrophobicity of three Ti-Beta zeolites saturated with water vapor.^{10,11} The sample adsorbing more water exhibited higher hydrophilicity.¹⁰ Thus, as shown in Fig. S12, the hydrophilicity of Ti-Beta-PS-100 was superior to that of Ti-Beta-HT-0.5-100, far beyond than that of Ti-Beta-F-100.

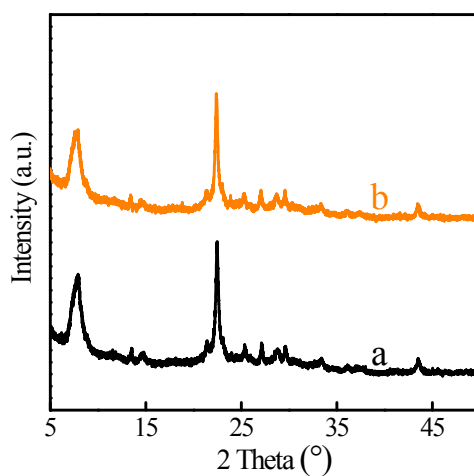


Fig. S13 XRD patterns of fresh (a) and the fourth run followed by calcination (b) for Ti-Beta-HT-0.5-50.

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