Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Hydroxyl free radical route to the stable siliceous Ti-UTL with extra-large pores for oxidative desulfurization

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Experimental Section

Synthesis of Ti-UTL

All the raw materials for the synthesis of Ti-UTL were commercially available. (6R,10S)-6,10-dimethyl-5-azoniaspiro[4.5]decane hydroxide as the structure directing agent (SDA) of Ti-UTL was prepared by the Ref.[1] The Ti-UTL was hydrothermally synthesized from a mixture of fumed silica (Aladdin Industrial Corporation), germanium dioxide (GeO_2, China Germanium Co. Ltd, 99.999%), titanium butoxide (TBOT, Macklin Co. Ltd), SDA and distilled water. In a typical synthesis, the SDA aqueous solution was diluted with water and GeO_2 were added under stirring. After 20 minutes, the fumed silica was dispersed in the solution under stirring. Then, TBOT (diluted 1:3 with 1-butanol) was added dropwise into the homogeneous solution until the TBOT hydrolysis completely. The molar composition of gel was 0.3 SDA: 0.5 GeO_2:1 SiO_2: 0.02 TBOT: 30 H_2O. Later, the gel was transferred into a 50 ml Teflon-lined autoclave and heated at 448 K for 7 days under stirring. The final product was filtrated, washed with distilled water and ethanol, dried at 353 K for 10 hours. Then, the sample was calcined at 823 K for 12 hours with a temperature ramp of 1°C/min.

Post-synthesis of calcined Ti-UTL

The post-synthesis treatment conducted under ultraviolet (UV) irradiation is referred to as UV condition, and control experiment conducted without UV irradiation is referred to as dark condition. Besides, the condition of using the H_2O_2 solution for the generation of ·OH is referred to as H_2O_2 condition.

Under UV conditions, 0.1 g Ti-UTL zeolites were added into the 6 g distilled water in the quartz Erlenmeyer flask (25 mL) and added a certain amount of tetraethyl orthosilicate (TEOS) which the molar ratio of TEOS and GeO_2 (containing in Ti-UTL) between 1 and 10. Then, the mixture was placed in the UV lamp (irradiance on the mixture: 65.0 mW/cm^2) with agitation for 3 hours at room temperature. Afterwards, the sample was filtrated, washed with distilled water and ethanol, dried at 353 K for 5 hours. The whole process was repeated once again, and the final products gotten.

Under H_2O_2 conditions, 0.1 g Ti-UTL zeolites and 60 uL 30% H_2O_2 aqueous solution were added into the 6 g distilled water in the beaker. Then, a certain amount of TEOS ($n(TEOS)/n(GeO_2) = 1\text{-}10$) was added in the solution under agitation for 3 hours at room temperature in the dark box. Afterwards, the sample was filtrated, washed with distilled water and ethanol, dried at 353 K for 5 hours. The whole process was repeated once again, and the final products were gotten.

Under dark conditions, the procedure was the same as the H_2O_2 condition without adding the H_2O_2 aqueous solution.

Post-synthesis Ti-UTL hydrolytic stability test

To verify the stability of post-synthesis Ti-UTL zeolites, the samples were immersed in the 0.2 M HNO_3 aqueous solution with a solid-to-liquid ratio of 1:100 at room temperature for 12 hours as the acid treatment. Then, the products were filtrated, washed with distilled water and ethanol, dried at 353 K for 5 hours. Later, all samples were calcined at 823 K for 5 hours with a temperature ramp of 2°C/min.

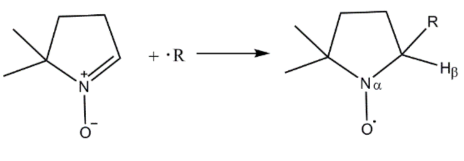
Catalytic oxidation reactions

The titanosilicate catalysts were all calcined at 823 K for 5 hours before being used in the catalytic reactions. A certain amount of dibenzothiophene (DBT) or dimethyldibenzothiophene (4,6-DMDBT) was dissolved in n-octane to act as a model fuel, and the concentration of reactant was 1000 ug/ml. The oxidations of model fuel were carried out in a 25 ml glass flask equipped with an Allihn condenser under intensive stirring (1000 rpm). In a typical run, 10 mg catalysts, 5 mL model fuel and a suitable amount of *tert*-butylhydroperoxide (TBHP) were mixed in the round-bottomed flask and stirred vigorously at 333 K for 2 hours. The molar ratio of TBHP to sulfide was 5. All reaction mixture was analyzed by GC analysis (Shimadzu GC-2014) to determine the conversion.

Characterization

Normal powder X-ray diffraction (PXRD) data were obtained by a Rigaku D/max-2000 diffractometer equipped with a graphite monochromator and using a Cu Kα (λ = 1.5418 Å). The data were collected at room temperature over the 3-35° 2θ range using a scan speed of 6° min^{-1}. The high resolution PXRD data were obtained using a PANalytical Empyrean diffractometer in the transmission mode (Debye–Scherrer geometry). The scan 2*θ* range was from 5° to 100° with a step size of 0.013° and a total data collection time of 12 hours. The solid-state ^{29}Si MAS NMR spectra were recorded on Bruker AVANCE III 400 MHz WB spectrometer with a Bruker 4 mm MAS probe at a resonance frequency of 79.5 MHZ with a spinning rate of 5 kHz, a 90° pulse width of 5 μs, and a recycle delay of 100 s. Surface area and pore volume were measured by nitrogen isotherms at 77 K on a Micromeritics ASAP 2020 analyzer after evacuation at 473 K for 8 hours. Inductively coupled plasma (ICP-OES) analyses were carried out on a Leeman Prodigy 7 ICP instrument. The morphology and size of the crystals were examined by a scanning electron microscopy (SEM) using a Hitachi S-4800 field emission scanning electron microscope. The UV-visible diffuse reflectance data were analyzed by a Shimadzu UV3600Plus spectrophotometer. The Fourier transform infrared (FTIR) spectra of zeolites were collected on a VERTEX 80V FT-IR instrument. The products were analyzed by gas chromatography-mass spectrometry (Agilent 5976C GC-MSD) and GC analysis (Shimadzu GC-2014). The EPR spectra were recorded on a Bruker Elexsys E580 spectrometer. General instrument settings were as follows: scanning frequency: 9.85 GHz; central field: 3520 G; scanning width: 100 G; scanning power: 9.5 mW; scanning temperature: 293 K.

DMPO trappings were explained in the following reaction:



The hyperfine coupling constants (HFCs) of the nitrogen and *β*-proton (a_N and $a_{H\beta}$) were given in the main text when referred.

UV conditions: 0.05 g Ti-UTL zeolites were added into the 3 g distilled water in the beaker and added 0.1054 g TEOS with agitation. The 200 μL of the mixture was added into 200 μL of aqueous DMPO solution with the concentration of 80 mM in the quartz cell. The sample was exposed to UV irradiation for one minute before the collection of EPR data.

H_2O_2 conditions: 0.05 g Ti-UTL zeolites, 30 uL 30% H_2O_2 aqueous solution and 0.1054 g TEOS were added into the 3 g distilled water in the beaker with agitation. After 3 h reaction, the 200 μL of the mixture was added into 200 μL of aqueous DMPO solution with the concentration of 80 mM in the quartz cell. Then, the EPR measurement was started.

Dark conditions: the procedure was the same as H_2O_2 condition without adding H_2O_2 aqueous solution.

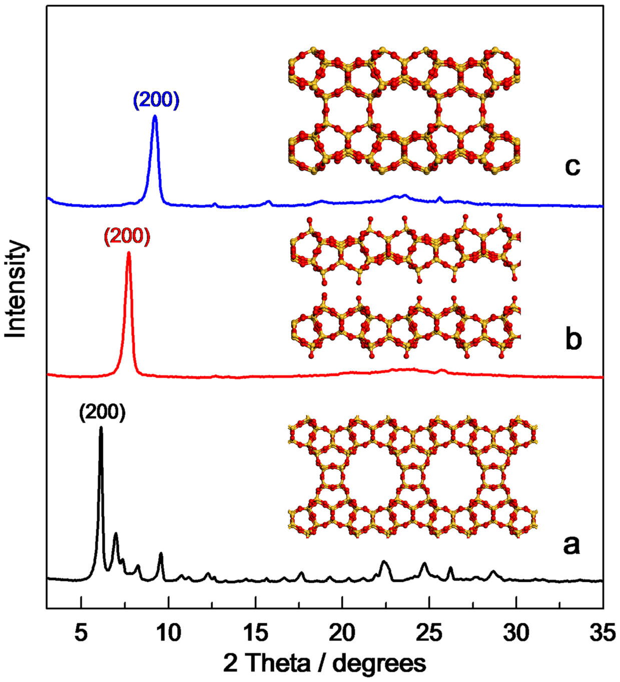


Fig. S1 Powder XRD patterns of (a) the calcined Ge-rich Ti-UTL, (b) after acid treatment, and (c) after further calcination[a].

[a] The acid treatment conditions are the same as the stability test.

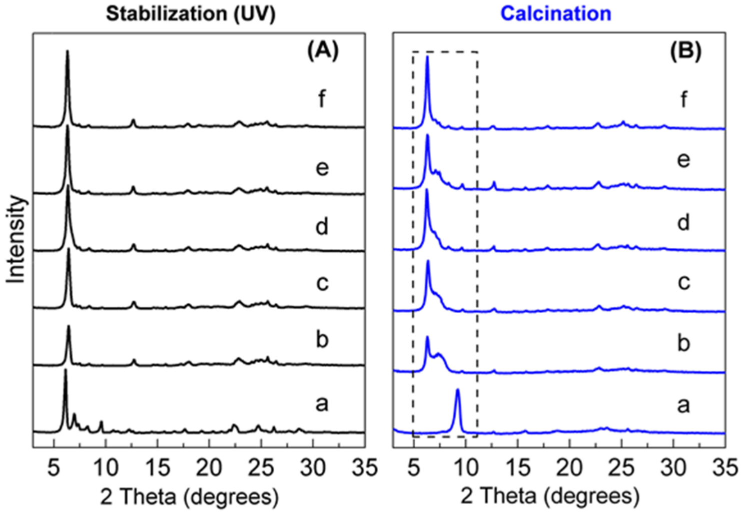


Fig. S2 PXRD patterns of (A) the parent sample and treated samples with TEOS/GeO_2 molar ratio of 2.5 obtained under UV condition: (a) parent Ti-UTL and stabilization with UV irradiation density of (b) 2, (c) 4, (d) 10, (e) 20 and (f) 30 mW/cm^2. (B)The PXRD patterns of the parent and treated samples after calcination.

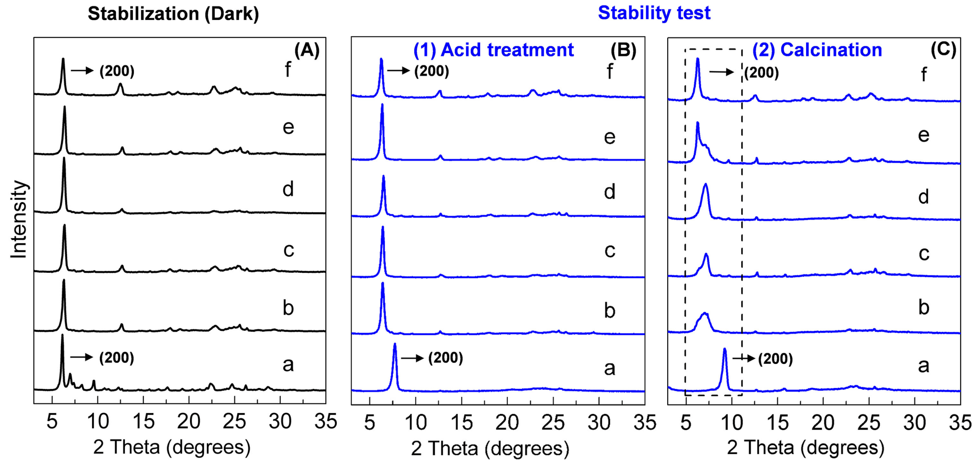


Fig. S3 PXRD patterns of the (A) parent sample and treated samples obtained under dark condition: (a) parent Ti-UTL and stabilization with TEOS/GeO_2 molar ratio of (b) 1, (c) 2, (d) 2.5, (e) 5 and (f) 10. The PXRD patterns of the parent and treated samples in stability test upon (B) acid treatment and (C) calcination.

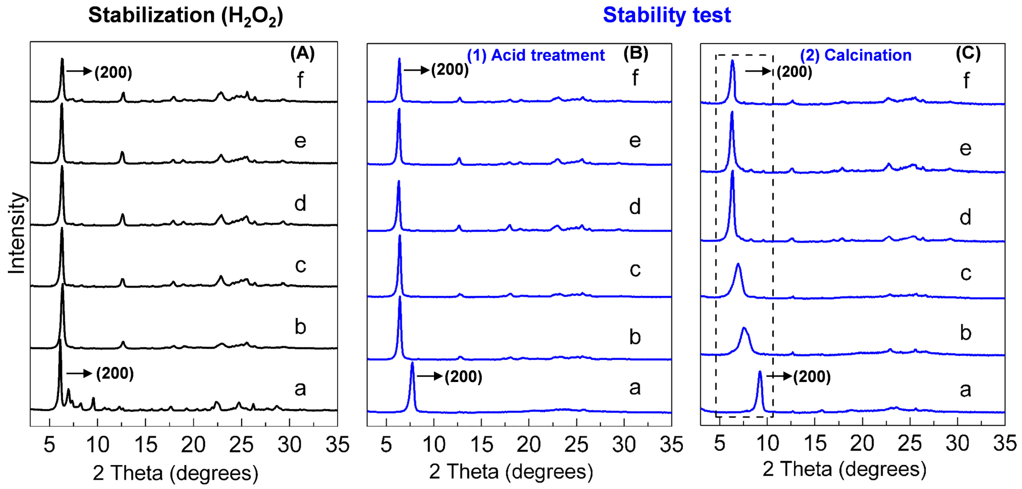


Fig. S4 PXRD patterns of (A) the parent sample and treated samples obtained under H_2O_2 condition: (a) parent Ti-UTL and stabilization with TEOS/GeO_2 molar ratio of (b) 1, (c) 2, (d) 2.5, (e) 5 and (f) 10. The PXRD patterns of the parent and treated samples in stability test upon (B) acid treatment and (C) calcination.

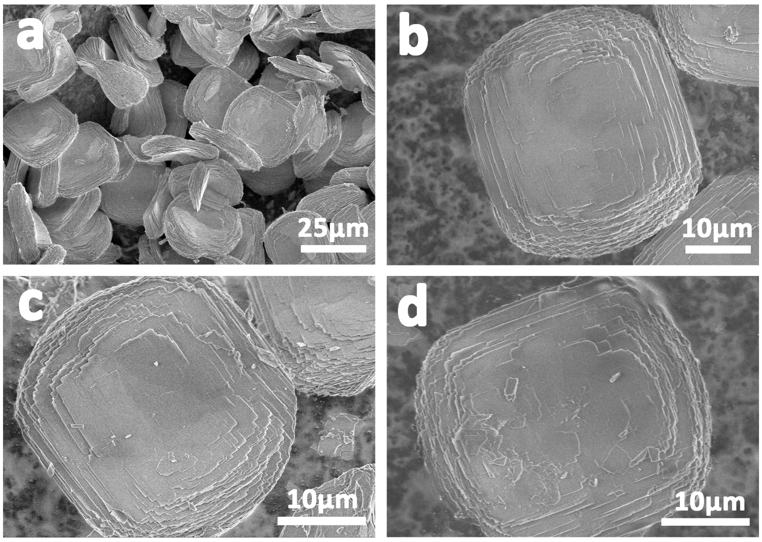


Fig. S5 SEM images of (a-b) the parent calcined Ti-UTL, the stabilized Ti-UTL with TEOS/GeO_2 molar ratio of 2.5 under (c) UV condition and (d) H_2O_2 condition.

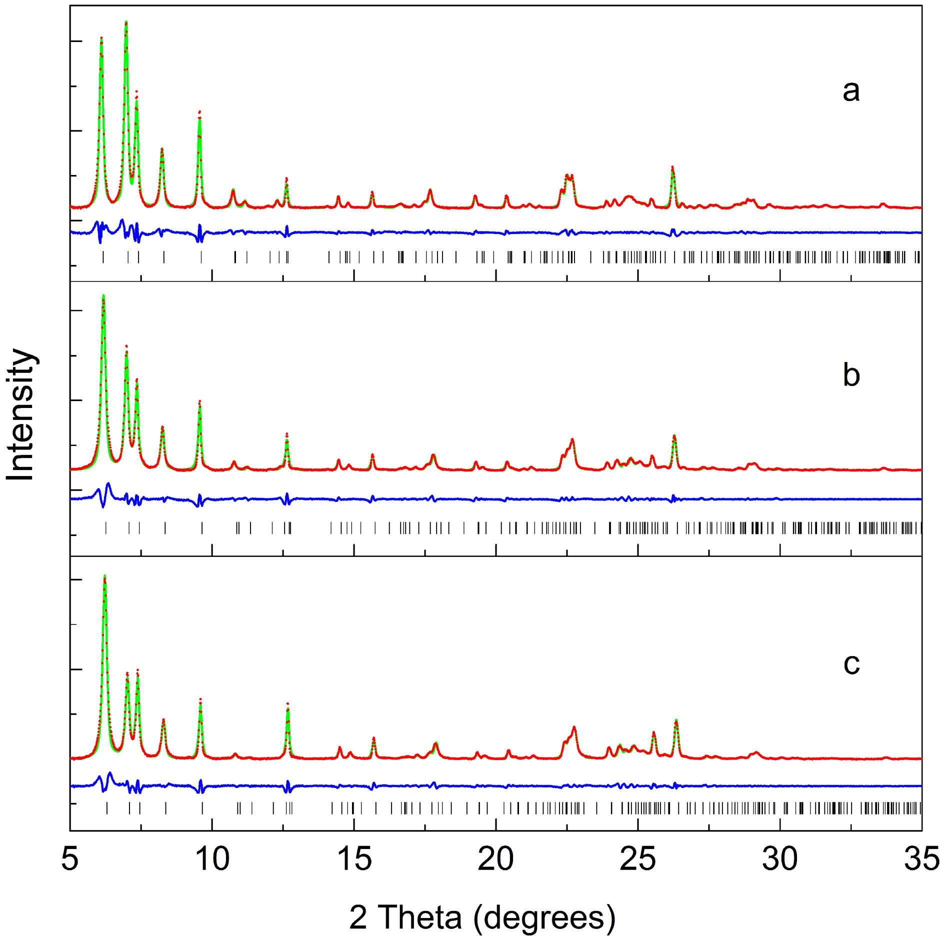


Fig. S6 The Le Bail fitting of powder X-ray diffraction for (a) the parent calcined Ti-UTL, (b) the stabilized Ti-UTL under H_2O_2 condition and (c) the stabilized Ti-UTL under UV condition. Red crosses represent the observed profiles; the green line indicates the simulated profile; the blue curve is the difference profile; the black bars indicate the positions of Bragg peaks.

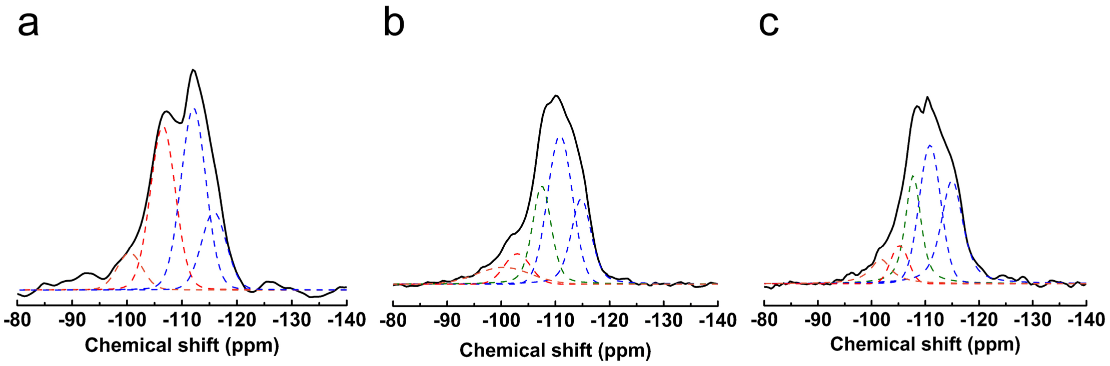


Fig. S7 ^{29}Si MAS NMR spectra of (a) the parent calcined Ti-UTL, the stabilized Ti-UTL with TEOS/GeO_2 molar ratio of 2.5 under (b) UV condition and (c) H_2O_2 condition.

The solid-state ^{29}Si MAS NMR spectra of the UTL zeolites exhibited several signals between δ = -100 and -120 ppm that represented the different chemical environments of silicon atoms in the framework. For germanosilicate zeolites, it was universally accepted that chemical shifts in the range of δ = -110 to -116 ppm were assigned to $Si(OSi)_4$ (Q^4) sites, those in the range δ = -100 to -110 ppm were attributed to nSi(4-n)Ge sites and those between δ = -90 to -100 ppm to $Si(OSi)_3(OH)$ (Q^3).[2,3] The resonance peaks at -115.8 ppm and -112.0 ppm in ^{29}Si MAS NMR spectra of Ti-UTL can be attributed to Q^4 sites, and those at -106.5 ppm and -100.5 ppm were assigned to 2Si2Ge and 1Si3Ge sites respectively. As for stabilized Ti-UTL (UV) and Ti-UTL (H_2O_2), those peaks corresponding to $(SiO)_nSi(GeO)_{4-n}$ (n= 2 to 4) sites were decreased due to the dropping out of Ge atoms while the resonance peaks shifted to lower field where the peaks belonging to the Si atoms locating in the *d4r* units, proving the substitution of Si for Ge in the framework during the stabilization process. Hence, signals at -107.5 ppm and -107.7 ppm separately were attributed to the Si atoms in the *d4r* units, which were mainly appearing in the range of -107.5 ppm to 109.5 ppm.[2]

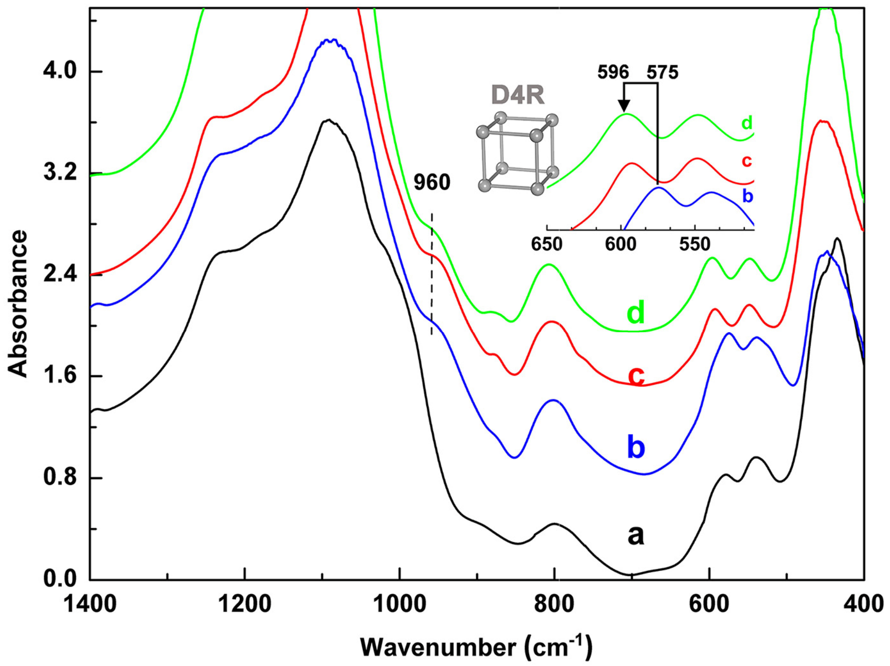


Fig. S8 FT-IR spectra of calcined (a) Ti-free UTL, (b) the parent Ti-UTL, the stabilized Ti-UTL with TEOS/GeO_2 molar ratio of 2.5 under UV condition (c) and H_2O_2 condition (d).

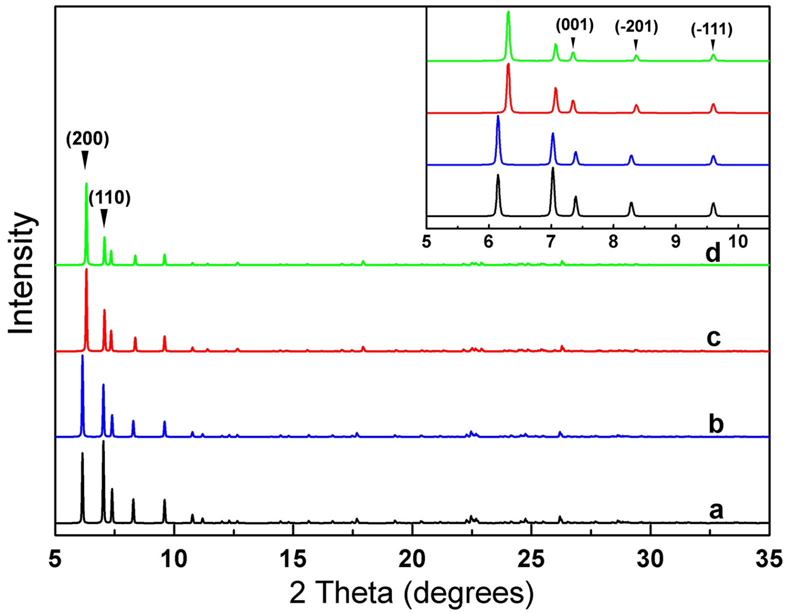


Fig. S9 Simulated PXRD patterns of Ti-UTL with the *d4r* structural units consisting of (a) 8Ge, (b)2Si6Ge, (c) 6Si2Ge and (d) 8Si.

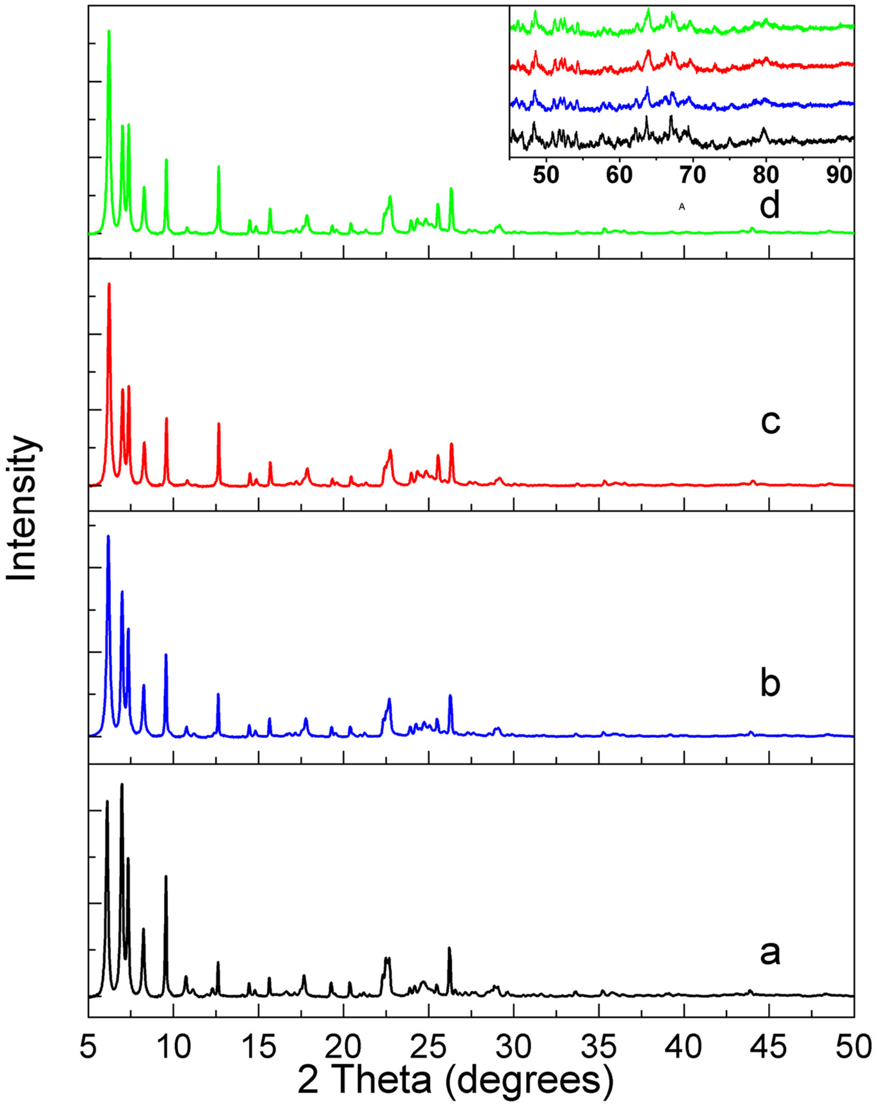


Fig. S10 PXRD patterns of (a) the parent calcined Ti-UTL, the stabilized Ti-UTL (b) under H_2O_2 condition, (c) under UV condition and (d) under dark condition.

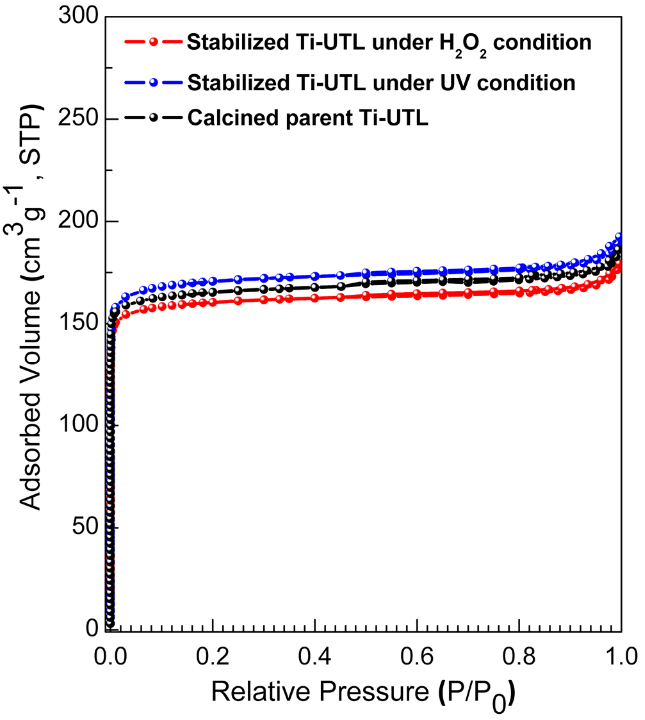


Fig. S11 N_2 adsorption isotherms measured at 77 K of the parent calcined Ti-UTL, the stabilized Ti-UTL with TEOS/GeO_2 molar ratio of 2.5 under UV condition and H_2O_2 condition.

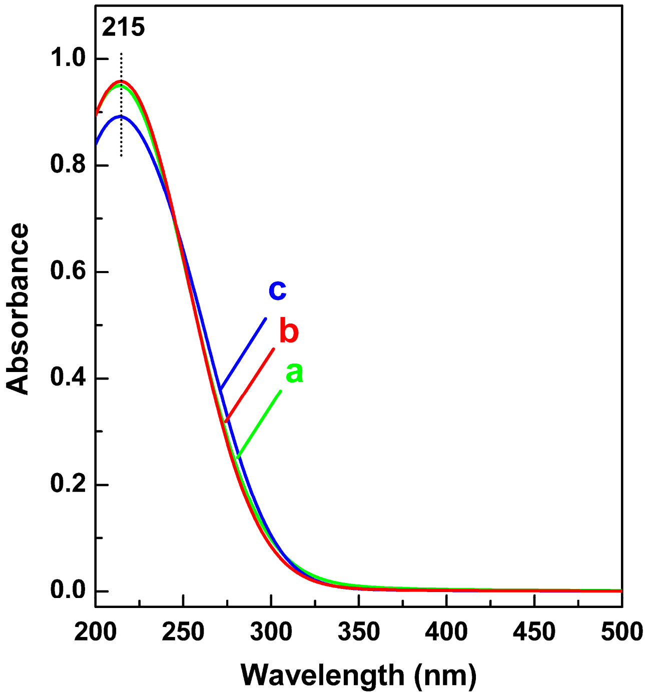


Fig. S12 UV-vis spectra of (a) the parent calcined Ti-UTL, the stabilized Ti-UTL with TEOS/GeO_2 molar ratio of 2.5 under (b) UV condition and (c) H_2O_2 condition.

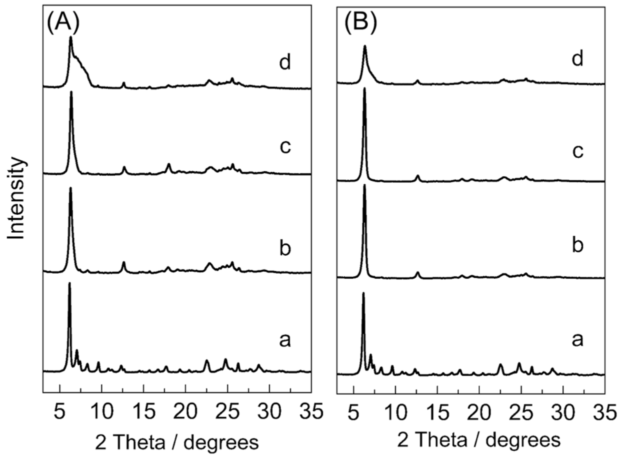


Fig. S13 PXRD patterns of the samples treated under (A) UV condition and (B) H_2O_2 condition. (a) the parent Ti-UTL, (b) treated with propanetriol, and after stability test including (c) acid washing (d) further calcination.

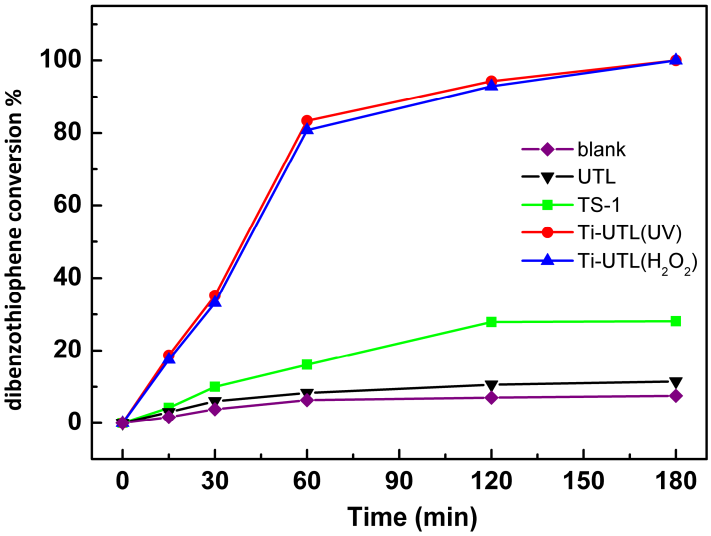


Fig. S14 Catalytic oxidation of DBT with TBHP over stabilized UTL, TS-1, stabilized Ti-UTL (UV), stabilized Ti-UTL (H_2O_2) zeolite catalysts.

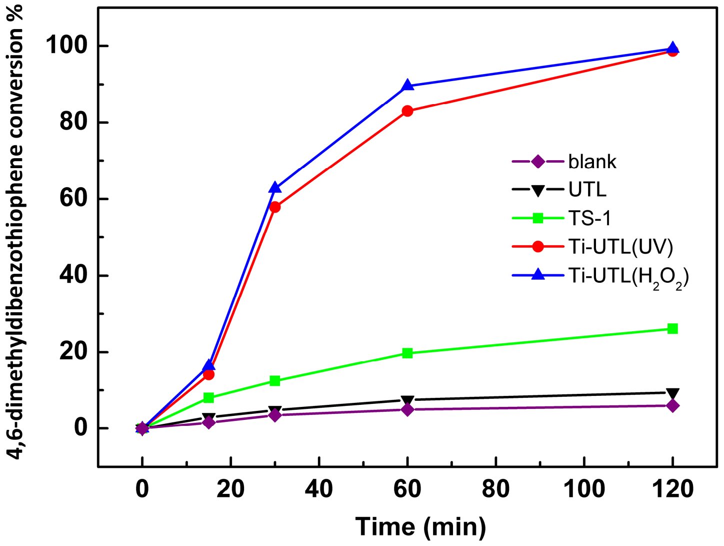


Fig. S15 Catalytic oxidation of 4,6-DMDBT with TBHP over stabilized UTL, TS-1, stabilized Ti-UTL (UV), stabilized Ti-UTL (H_2O_2) zeolite catalysts.

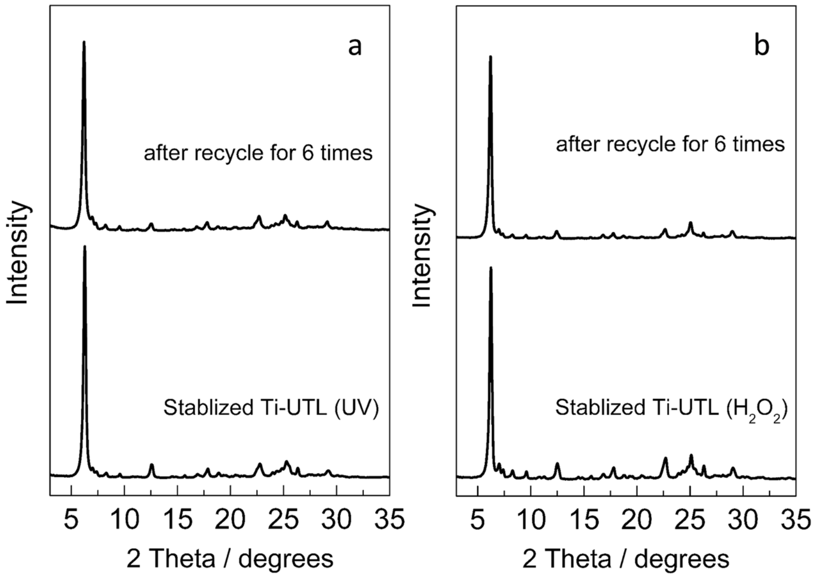


Fig. S16 PXRD patterns of (a) the fresh and recycled six times of the stabilized Ti-UTL (UV), (b) the fresh and recycled six times of the stabilized Ti-UTL (H_2O_2) in the ODS of DBT.

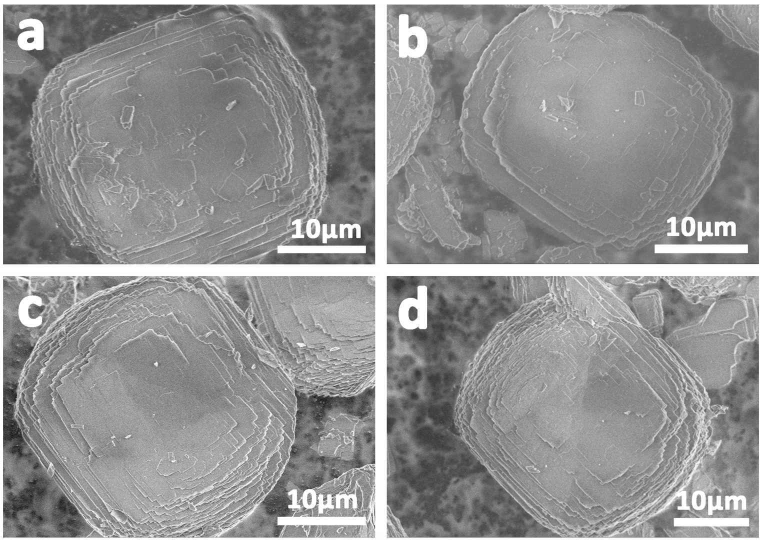


Fig. S17 SEM images of (a) fresh stabilized Ti-UTL (UV), (b) recycled six times of the stabilized Ti-UTL (UV), (c) fresh stabilized Ti-UTL (H_2O_2), (d) recycled six times of the stabilized Ti-UTL (H_2O_2).

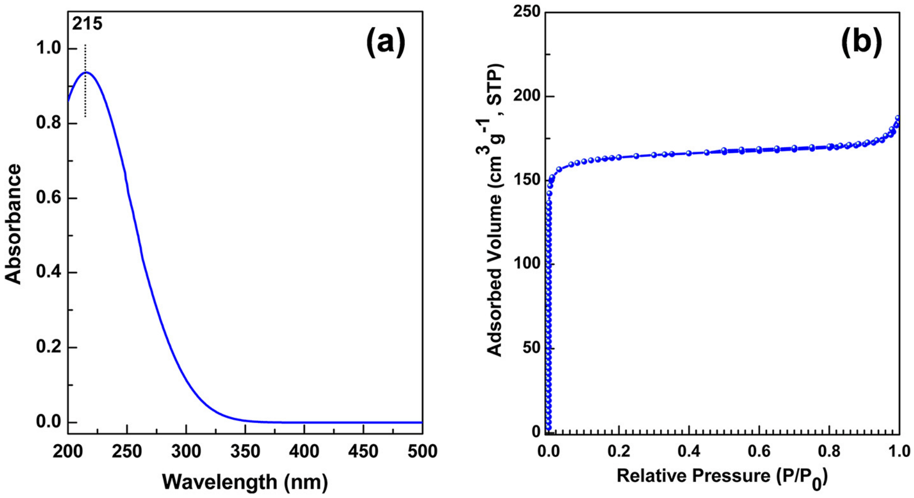


Fig.S18 (a) UV-vis spectrum and (b) N_2 adsorption isotherms of the stabilized Ti-UTL (UV) after six cycles in the oxidation of DBT.

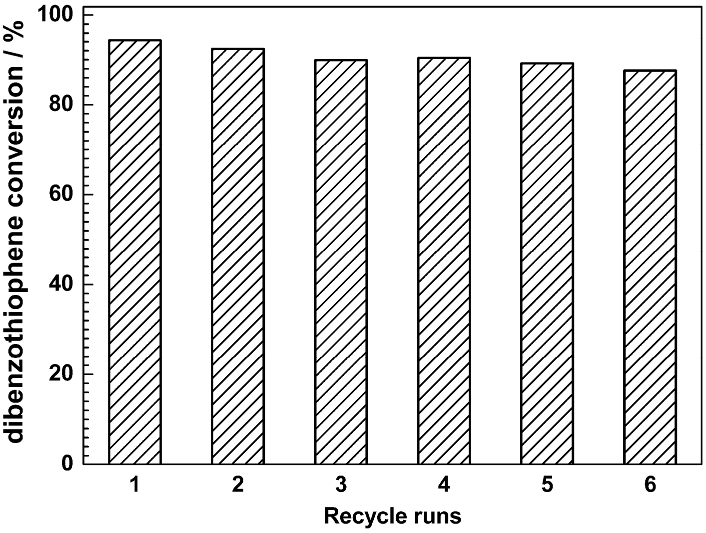


Fig. S19 Recycle test in the oxidation of DBT with TBHP over the stabilized Ti-UTL zeolite catalysts (stabilized with UV irradiation).

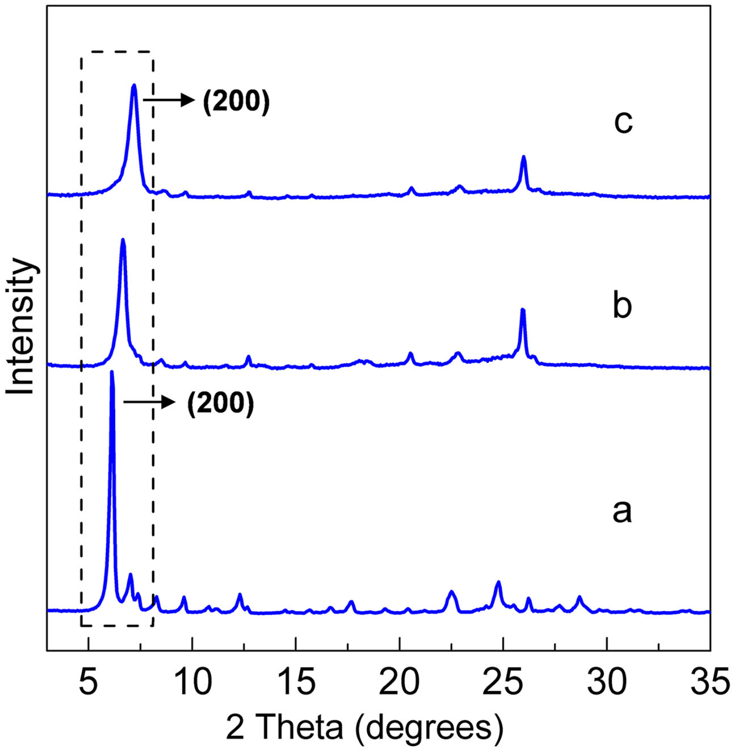


Fig. S20 PXRD patterns of (a) the parent Ti-UTL without stabilization, (b) after catalytic oxidation of DBT and (c) further calcination.

Table S1. Physiochemical property of the parent and the stabilized Ti-UTL.

Sample	S_{BET} [a] $[m^2g^{-1}]$	S_{ext} [b] $[m^2g^{-1}]$	S_{micro} [c] $[m^2g^{-1}]$	V_{micro} [b] $[cm^3g^{-1}]$	V_{pore} [d] $[cm^3g^{-1}]$
Ti-UTL	556	54	502	0.23	0.28
Ti-UTL (H_2O_2)	539	47	492	0.23	0.27
Ti-UTL (UV)	571	57	514	0.24	0.29

[a] The surface area was calculated by BET method. [b] The micropore volume and external surface area were calculated by *t*-Plot method. [c] The micropore surface area was calculated by the equation of $S_{micro} = S_{BET} - S_{exter}$. [d] The total pore volume was calculated by the adsorption data at $P/P_o = 0.974$.

Table S2. Oxidative desulfurization of DBT and 4,6-DMDBT over various titanosilicate[a].

Catalyst	Si/Ti[b]	Sulfur compound	Conv. (%)[c]
Ti-Beta	52	DBT	96.2
		4,6-DMDBT	68.4
Ti-MWW	40	DBT	100
		4,6-DMDBT	100

[a] Reaction conditions: 5 mL 1000 ug/mL model fuels, 60℃, 10 mg catalysts, 30 uL 65% TBHP. [b] Measured by inductively coupled plasma (ICP). [c] After 2 hours of the catalytic reaction.

Table S3. The element analyses of the stabilized Ti-UTL (UV) after recycle test.

Sample	Si/Ge[b]	Si/Ti[b]
Ti-UTL (UV)	30.1	119.2
Ti-UTL (UV&six)[a]	30.1	121.6

[a] the stabilized Ti-UTL (UV) after six cycles in the oxidation of DBT.

[b] Measured by inductively coupled plasma (ICP).

Table S4. Oxidative desulfurization of DBT over Ti-UTL without stabilization[a].

			Conv. (%)	
Samples	Si/Ge[d]	Si/Ti[d]	DBT[e]	TON[f]
Ti-UTL[b]	3.9	105	42.1	10.1
Ti-UTL (Cat.)[c]	4.5	106	–	–

[a] Reaction conditions: 5 mL 1000 ug/mL model fuels, 60℃, 10 mg catalysts, 30 uL 65% TBHP. [b] the parent Ti-UTL without stabilization. [c] the parent Ti-UTL after catalytic oxidation of DBT. [d] Measured by inductively coupled plasma (ICP). [e] After 2 h of the catalytic reaction. [f] Turnover number (moles of converted DBT /mole of Ti sites).

Reference

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2 H. Xu, J.-g. Jiang, B. Yang, L. Zhang, M. He and P. Wu, *Angew. Chem. Int. Ed.*, 2013, **53**, 1355-1359.

3 W. H. Fu, Z. Yuan, Z. Wang, Y. Wang, W. Yang and M. Y. He, *Dalton Trans*, 2017, **46**, 6692-6699.