

Supplementary Information

One-pot synthesis of framework W-doped TS-1 zeolite with robust Lewis acidity for effective oxidative desulfurization

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Materials and methods

Reagents and chemicals

Tetrapropylammonium hydroxide (TPAOH, 25 wt%), tetraethyl orthosilicate (TEOS, 99%), tetrabutyl orthotitanate (TBOT, 99%), tungsten(VI) chloride (99.5%), hydrogen peroxide (H₂O₂, 30 wt%), tert-butyl hydroperoxide (TBHP, 70 wt%), dibenzothiophene (DBT, 99.5%) and benzothiophene (BT, 99.5%) were purchased from Shanghai Aladdin Chemical Reagents Co., Ltd. Isopropanol (99.5%) and n-octane (99.5%) were marketed by Tianjin Chemart Chemical Reagents Co., Ltd. 4,6-dimethyldibenzothiophene (4,6-DMDBT, 99.5%) was provided by Shanghai Aladdin Chemical Co., Ltd. Anatase titanium dioxide (TiO₂, 99.8%) was obtained from Shanghai Macklin Biochemical Co., Ltd. The purchased anatase TiO₂ has an rough and irregular crystal morphology as well as an average size of about 50 nm. Ultrapure deionized water used throughout has a resistivity of 18.2 MΩ·cm. All the aforementioned chemicals are used as received without further purification.

Preparation of W-MFI zeolite

In a typical procedure of W-MFI zeolite, 12.8 g of TPAOH and 3.2 g of deionized water are mixed together at room temperature, and then 6.7 g of TEOS is added into the aqueous mixture under vigorous stirring for 3 h to obtain a clear solution. Then, 0.145 g, 0.29 g or 0.435 g of tungsten(VI) chloride is dissolved in 3.0 g anhydrous ethanol with the aid of ultrasonic instrument, and is added dropwise into the above clear solution under vigorous stirring for 24 h at room temperature. Subsequently, the temperature is increased to 363 K to remove ethanol for 1 h. The molar composition of the final suspension is 1.0 SiO₂: m WO₃ (m = 0.0114, 0.228, 0.0342) : 0.5 TPAOH : 25 H₂O. Finally, the obtained precursor was poured into a 50 ml Teflon-lined stainless steel autoclave for hydrothermal synthesis in a homogeneous reactor at 373 K for 2 day under static conditions. The synthesized solid particles are recovered by centrifugation at 12000 rpm, washed with ethanol and deionized water for several times until pH 7.5 is reached, and then subjected to drying in a vacuum oven at 353 K for 12 h as well as calcination in air at 823 K for 6 h. The obtained W-MFI zeolite is labeled as WS(x) with Si/W molar ratio of x.

Preparation of Ti-MFI zeolite

In a typical procedure of Ti-MFI zeolite, 12.8 g of TPAOH and 3.2 g of deionized water are mixed together at room temperature, and then 6.7 g of TEOS is added into the aqueous mixture under vigorous stirring for 3 h to obtain a clear solution. Then, 0.125 g, 0.25 g or 0.375 g of TBOT is dissolved in 3.73 g of isopropanol with the aid of ultrasonic instrument, and is added dropwise into the above clear solution under vigorous stirring for 3 h at room temperature. Subsequently, the temperature is increased to 363 K to remove ethanol and isopropanol for 1 h. The molar composition of the final suspension is $1.0 \text{ SiO}_2 : n \text{ TiO}_2$ ($n = 0.0114, 0.228, 0.0342$) : 0.5 TPAOH : 25 H_2O . Finally, the obtained precursor was poured into a 50 ml Teflon-lined stainless steel autoclave for hydrothermal synthesis in a homogeneous reactor at 443 K for 2 day under static conditions. The synthesized solid particles are recovered by centrifugation at 12000 rpm, washed several times with deionized water and ethanol, and then subjected to drying in a vacuum oven at 353 K for 12 h as well as calcination in air at 823 K for 6 h. The obtained TS-1 zeolite is labeled as TS(x) with Si/Ti molar ratio of x.

Preparation of W-doped TS-1 zeolite

In a typical procedure of W-doped TS-1 zeolite, 12.8 g of TPAOH and 3.2 g of deionized water are mixed together at room temperature, and then 6.7 g of TEOS is added into the aqueous mixture under vigorous stirring for 3 h to obtain a clear solution. Then, 0.125 g, 0.25 g or 0.375 g of TBOT is dissolved in 3.73 g of isopropanol with the aid of ultrasonic instrument, and is added dropwise into the above clear solution under vigorous stirring for 3 h at room temperature. Subsequently, 0.145 g, 0.29 g or 0.435 g of tungsten(VI) chloride is dissolved in 3.0 g anhydrous ethanol with the aid of ultrasonic instrument, and is added dropwise into the above suspension under vigorous stirring for 24 h at room temperature. Then, the temperature is increased to 363 K to remove ethanol and isopropanol for 1 h. The molar composition of the final suspension is $1.0 \text{ SiO}_2 : n \text{ TiO}_2$ ($n = 0.0114, 0.228, 0.0342$) : $m \text{ WO}_3$ ($m = 0.0114, 0.228, 0.0342$) : 0.5 TPAOH : 25 H_2O . Finally, the obtained precursor was poured into a 50 ml Teflon-lined stainless steel autoclave for hydrothermal synthesis in a homogeneous reactor at 443 K for 2 day under static conditions. The synthesized solid particles are recovered by centrifugation at 12000 rpm, washed several times with deionized water and ethanol, and then subjected to drying in a

vacuum oven at 353 K for 12 h as well as calcination in air at 823 K for 6 h. The obtained W-doped TS-1 zeolite is labeled as WTS(x) with Ti/W molar ratio of x.

Preparation of crystalline WO₃

0.435 g tungsten(VI) chloride dissolved in 3.0 g anhydrous ethanol is added dropwise to a 16.0 g aqueous solution of 2 wt% tetrapropylammonium hydroxide (TPAOH) at room temperature under vigorous stirring. The obtained suspension was transferred into a Teflon-lined stainless steel autoclave and subjected to hydrothermal synthesis at 373 K for 1 day. After cooling to room temperature, the product was recovered by centrifugation, dried at 353 K in a vacuum oven overnight, and finally calcined at 823 K for 6 h.

Characterizations

The prepared zeolite crystal dimension and morphology were observed on a JEOL S-4800 field mission scanning electron microscope. The elemental composition and energy distribution of the obtained zeolite catalysts were analyzed by energy-dispersive X-ray spectroscopy (EDS). A JEOL JEM-2100 field mission transmission electron microscope was applied to image the zeolite catalysts at 200 KeV. X-ray photoelectron spectra (XPS) of the zeolite catalysts were generated on an ESCALAB 250Xi spectrometer equipped with an AlK α ($h\nu = 1486.6$ eV) X-ray radiation source with C 1s (284.6 eV) energy as a reference. X-ray diffraction (XRD) patterns of the zeolite catalysts were determined with an X-ray diffractometer (Bruker D8 Advanves) equipped with a Cu-K α radiation operated at a current of 40 mA and a voltage of 40 kV. Diffractograms were scanned in the 2θ range of 5° to 50° with a scanning speed of 8 °/min. IR spectra of the zeolite catalysts were recorded on a fourier transform infrared spectrometer (Nicolet-380) using KBr pellet technique. A UV-vis absorption spectrometer (Shimadzu UV 2550) was used to collect UV-vis DRS spectra of the zeolite catalysts in the wavenumber of 200 nm to 500 nm with BaSO₄ as the reference. Titanium and tungsten content of the zeolite samples were determined with a X-ray fluorescence (XRF) spectrometer (Bruker S4 Pioneer). UV-Raman spectra of the zeolite samples were collected with a Renishaw inVia Reflex Raman spectroscopy using a He-Cd laser line of 325 nm as excitation source. N₂ adsorption/desorption isotherms of the synthesized zeolite catalysts were performed on a SSA-7000 instrument at 77K after

pretreatment at 573 K for 3 h under vacuum. Brunauer-Emmett-Teller (BET) method was used to determine their specific surface area, t-plot method was applied in the calculation of their micropore volume and adsorption pore volume at $P/P_0 = 0.9988$ was recorded as their total pore volume. In addition, adsorption branch of their isotherms were utilized to calculate pore size distributions using a Barrett-Joyner-Halenda (BJH) model. Ammonia temperature-programmed desorption (NH_3 -TPD, CHEMBET 3000) were applied to study the acidities of the zeolite samples. The catalyst samples were pretreated at 773 K for 1 h in flowing He (40 mL/min). After cooled to 373 K, the zeolite samples were subjected to pure ammonia for adsorption of 30 min and subsequently the flowing He (40 mL/min) was passed through for an additional 30 min to remove excess ammonia. Subsequently, the TPD profiles were collected in the temperature of 373 K to 973 K with a heating rate of 10 K/min. The type and concentration of Lewis acid sites and Brønsted acid sites for the zeolite catalysts were evaluated by a Pyridine IR (Py-IR) spectrophotometer (Magna-IR 560 ESP). Zeolite catalysts were first pressed into a wafer and purged at 673 K for 3 h under a vacuum of 10^{-3} Pa. After cooled to room temperature, the zeolite sample was subjected to pure pyridine vapor for 30 min of adsorption and then evacuated for 1 h to remove the excess pyridine. Subsequently, the cell temperature was increased to 423 K and 623 K, and the corresponding Py-IR spectra were collected in the wavenumber of 1400 cm^{-1} to 1700 cm^{-1} .

Catalytic tests

0.175g of DBT, BT or 4,6-DMDBT were dissolved in 500 ml of n-octane to obtain the model fuel with a sulfur concentration of about 500 ppm. In a typical process, 100 mg of zeolite catalyst and 20 ml of model fuel were poured into a one-necked glass flask. The oxidation reaction was performed at 333 K under a stirring speed of 500 rpm. TBHP or H_2O_2 was used as the oxidant agent and the molar ratio of the oxidant with S-organic compound was set to 3. The solution was sampled regularly in the interval of 15 min from the flask and analyzed on a high-performance liquid chromatography (Shimadzu LC-2030). The oxidized S-compounds were quantified on an Agilent 7890/5975C-GC/MSD Gas chromatography/Mass spectrometry equipped with a HP-5 MS column (30 m long \times 250 μm inner diameter \times 0.25 μm film thickness). The removal rate (R) of sulfur compound in the

model fuel was calculated according to the following equation:

$$R = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

Where C_0 represents for the initial sulfur compound concentration and C_t refers to the sulfur compound concentration at a reaction time of t .

Supplementary figures and tables

Table S1. Element energy in KeV detected by EDS X-ray microanalysis.

Element	O K _α	Si K _α	Ti K _α	Ti L _α	W L _α	W M _α
Energy (KeV)	0.523	1.740	4.508	0.452	8.396	1.775

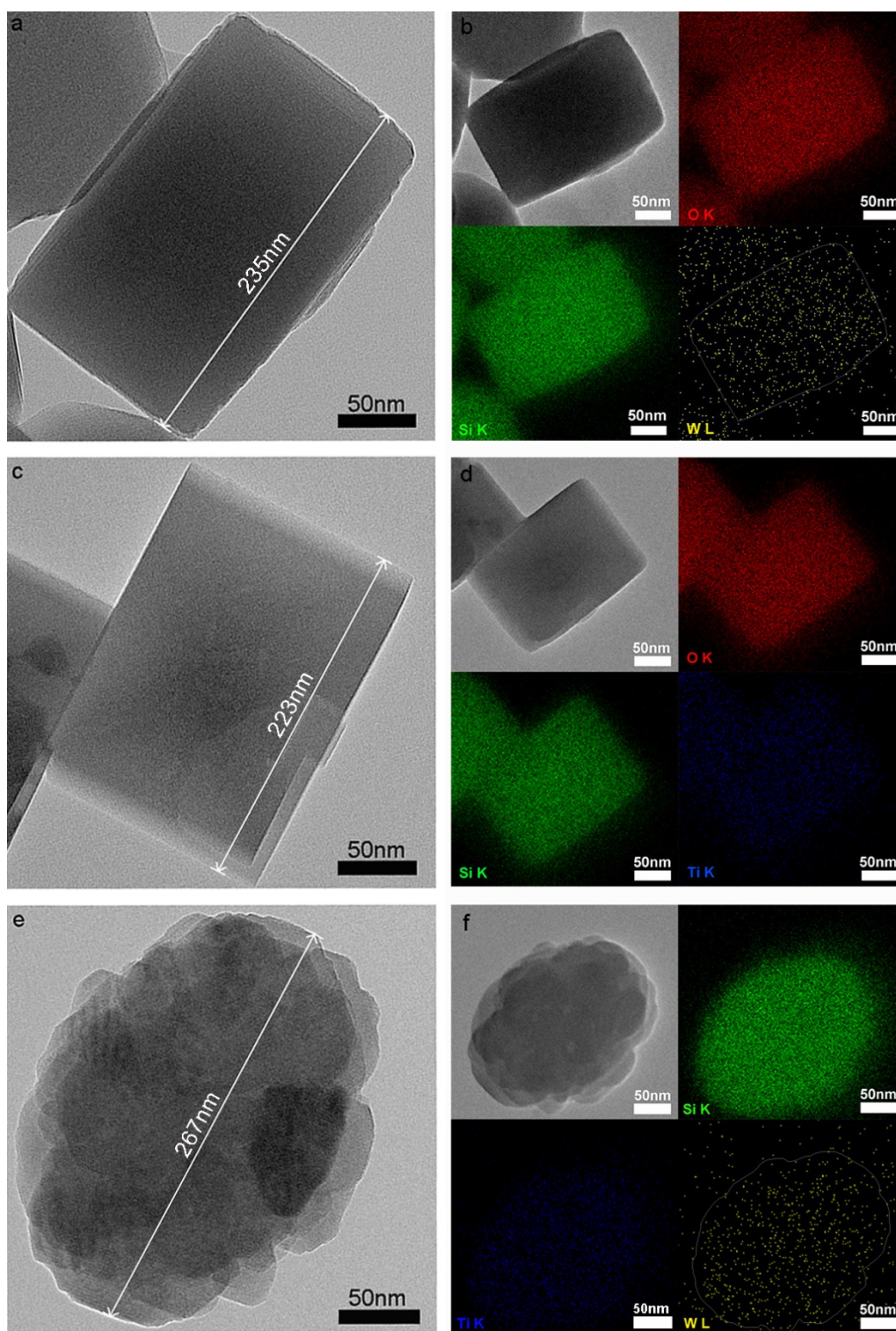
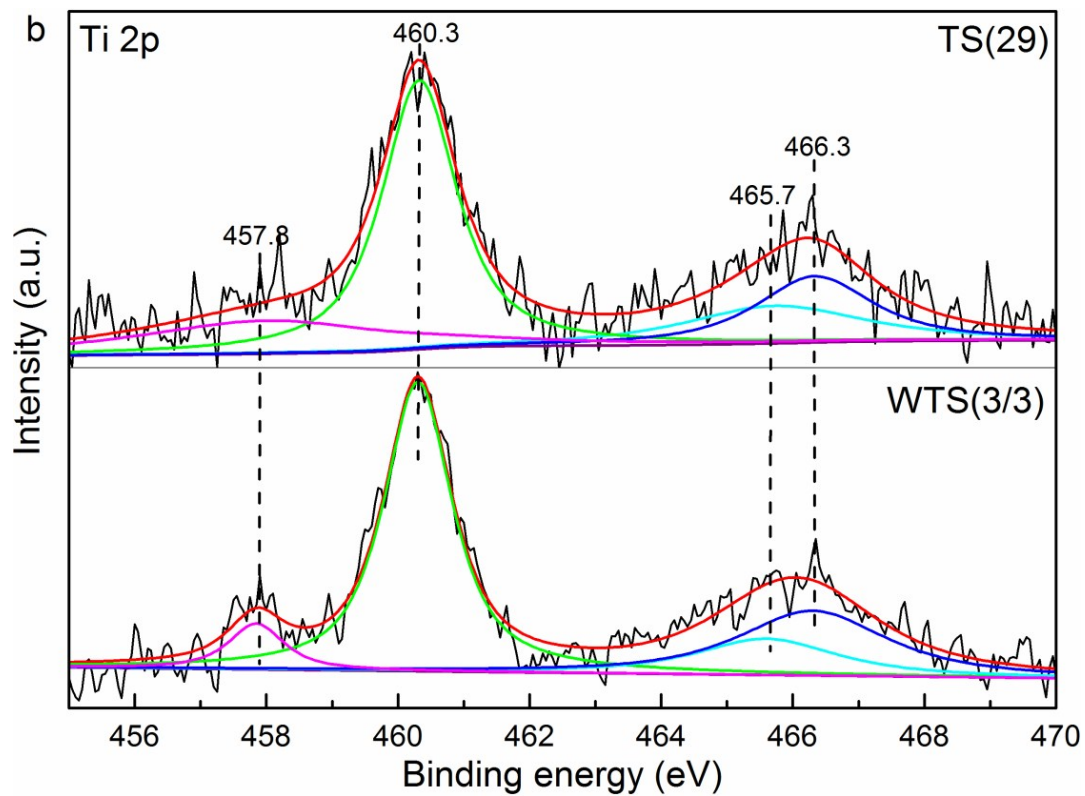
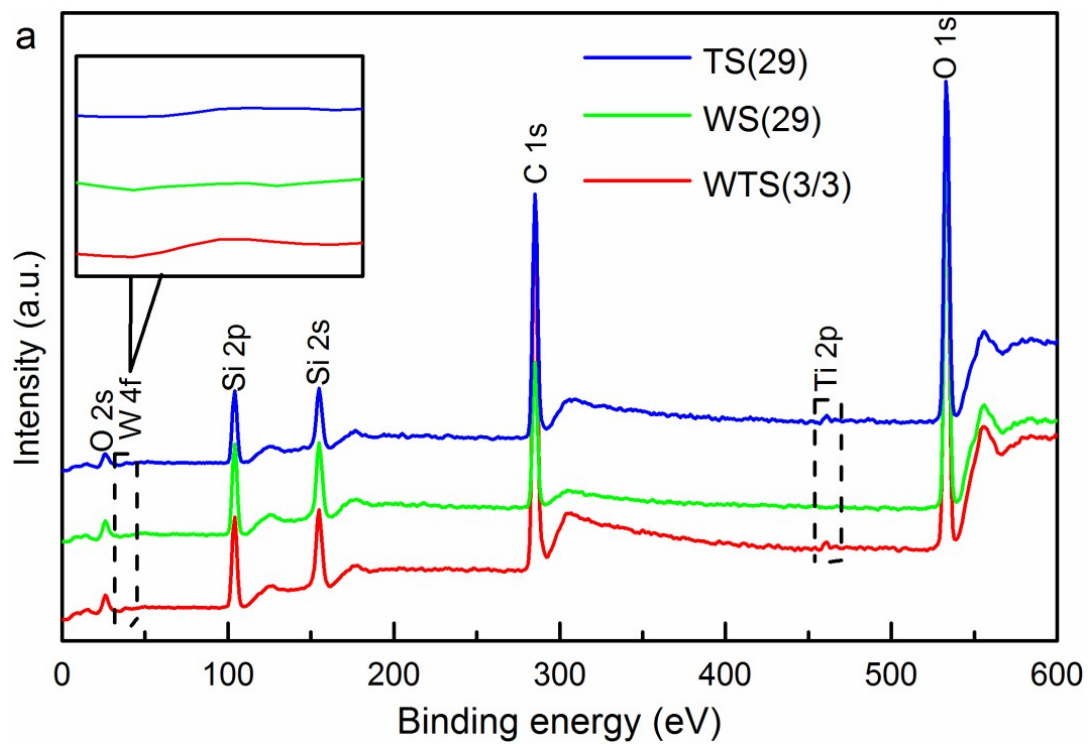


Figure S1. High magnification TEM images of the prepared W-MFI zeolite WS(29) (a), Ti-MFI zeolite TS(29) (c) and W-doped TS-1 zeolite WTS(3/3) (e) as well as their mapping analyses (b, d, f).



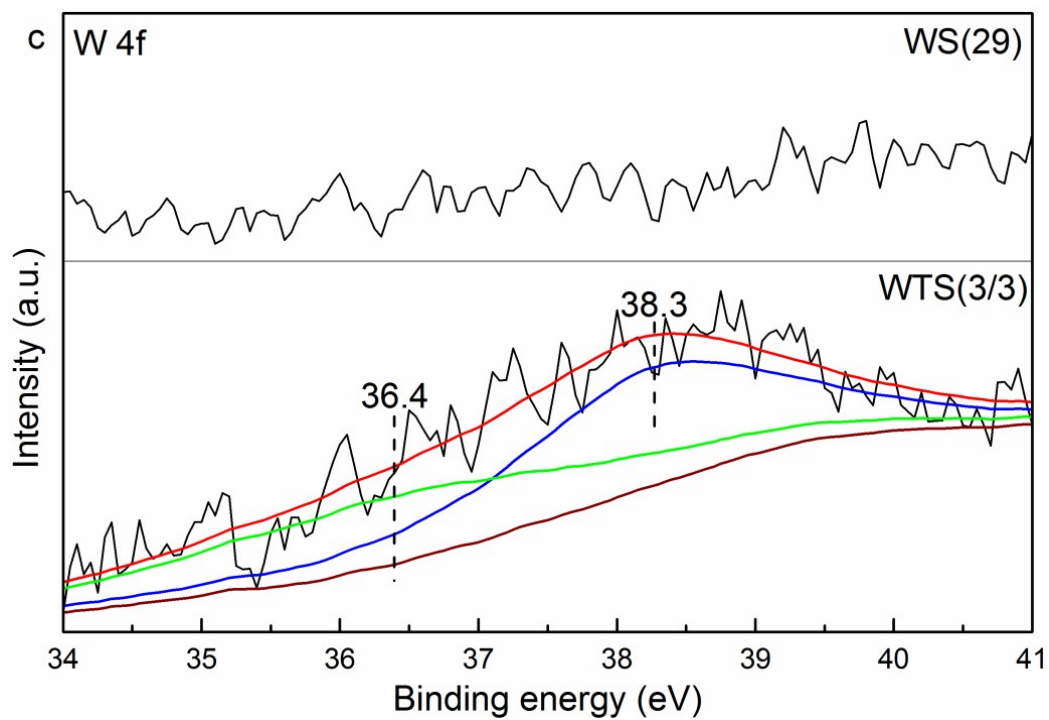


Figure S2. XPS spectra of W-MFI zeolite WS(29), Ti-MFI zeolite TS(29) and W-doped TS-1 zeolite WTS(3/3) (a), high-resolution Ti 2p XPS spectra of TS(29) and WTS(3/3) (b) as well as high-resolution W 4f XPS spectra of WS(29) and WTS(3/3) (c).

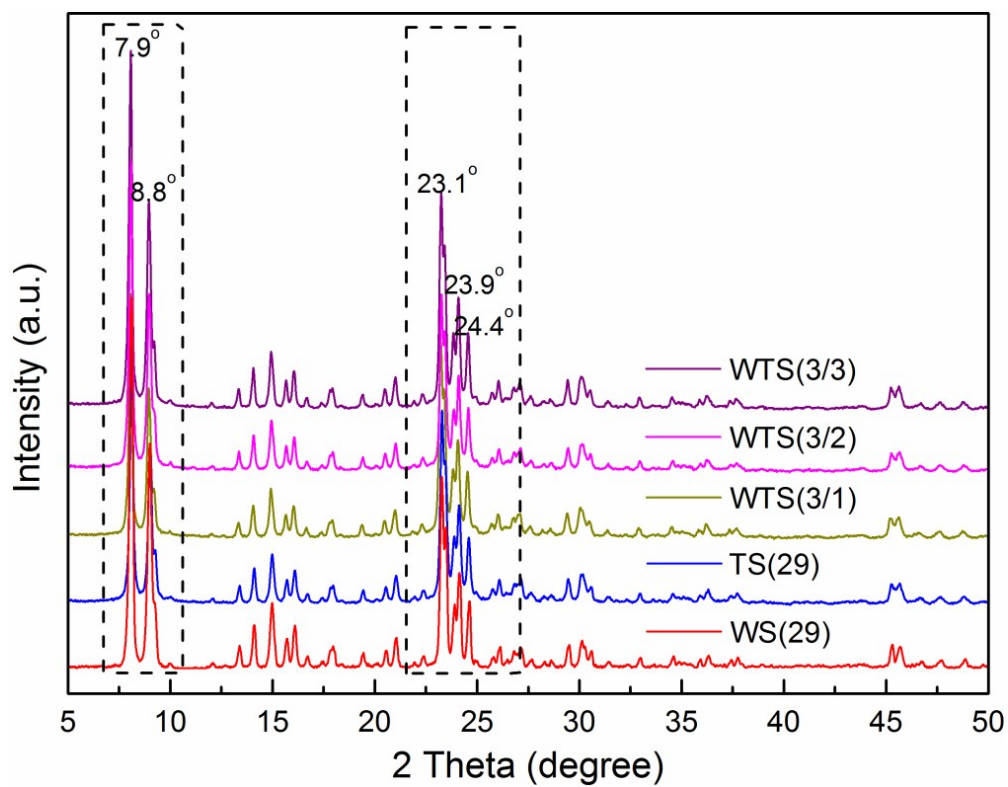


Figure S3. X-ray diffraction patterns of W-MFI zeolite WS(29), Ti-MFI zeolite TS(29) and W-doped TS-1 zeolite WTS(3/3).

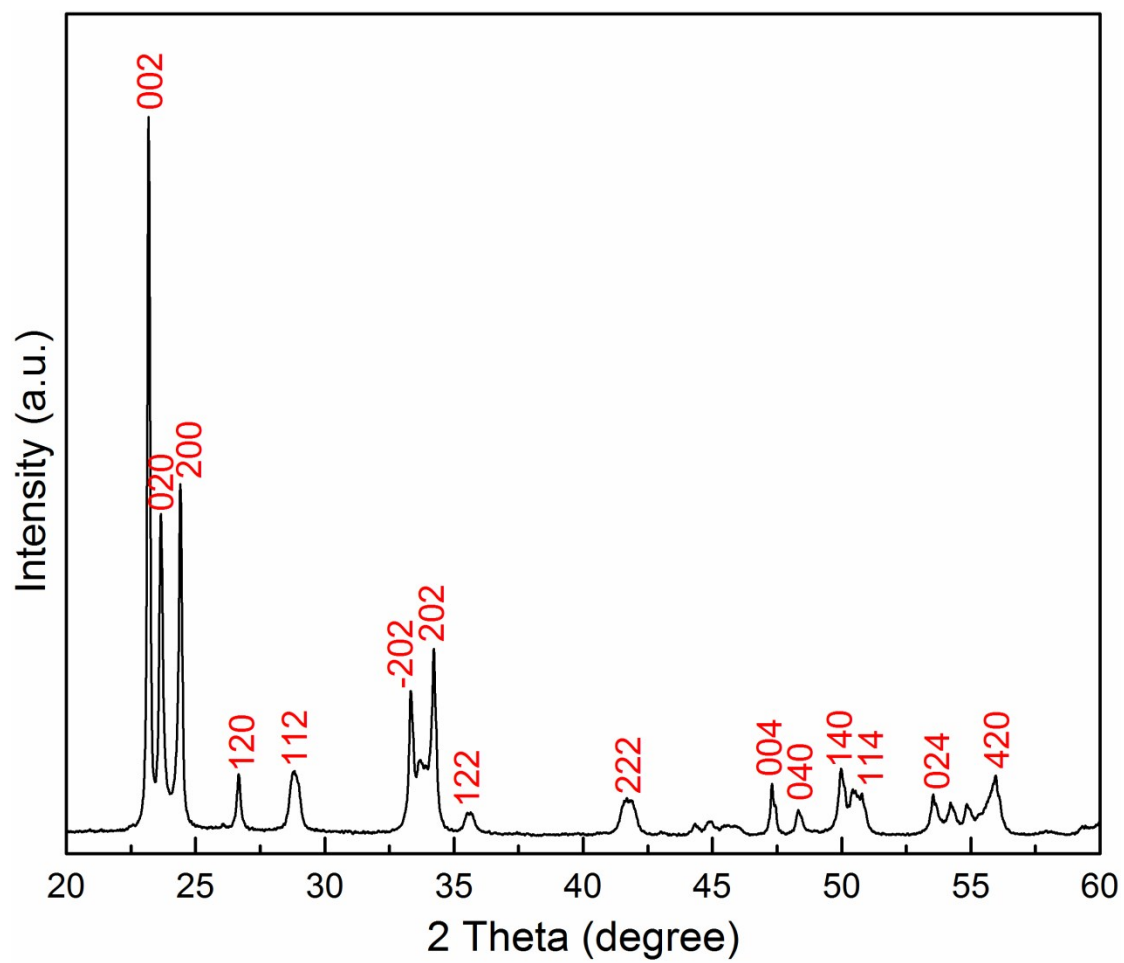


Figure S4. X-ray diffraction pattern of the prepared monoclinic WO_3 .

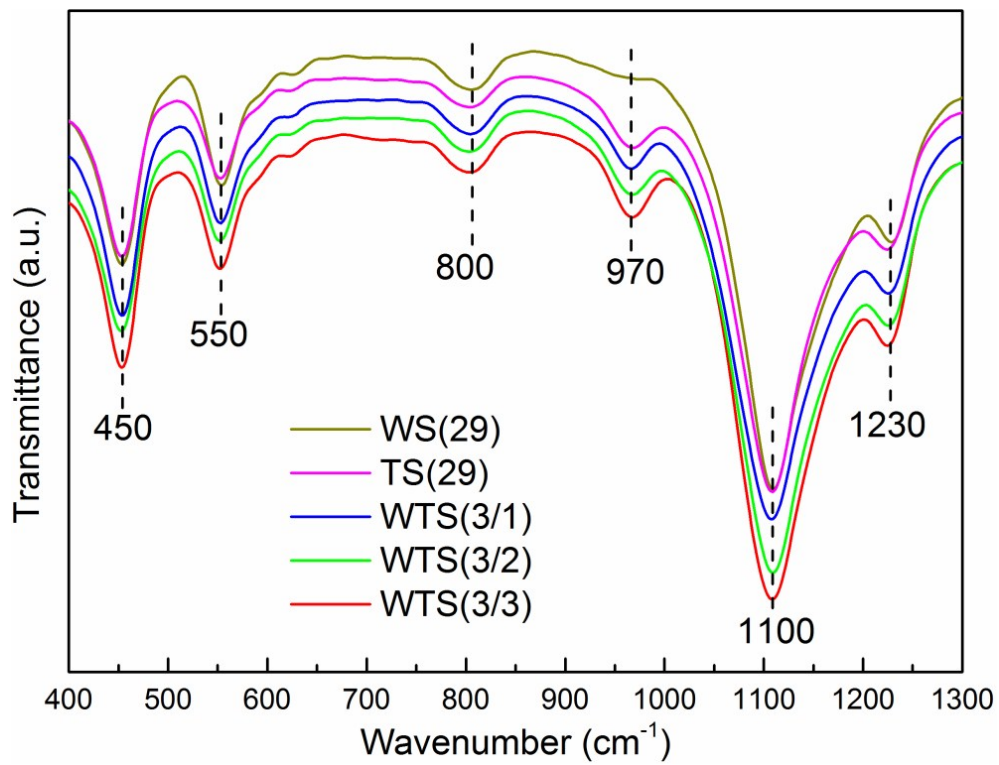


Figure S5. FTIR spectra of the prepared W-MFI zeolite WS(29), Ti-MFI zeolite TS(29) and W-doped TS-1 zeolite WTS(3/1), WTS(3/2), WTS(3/3).

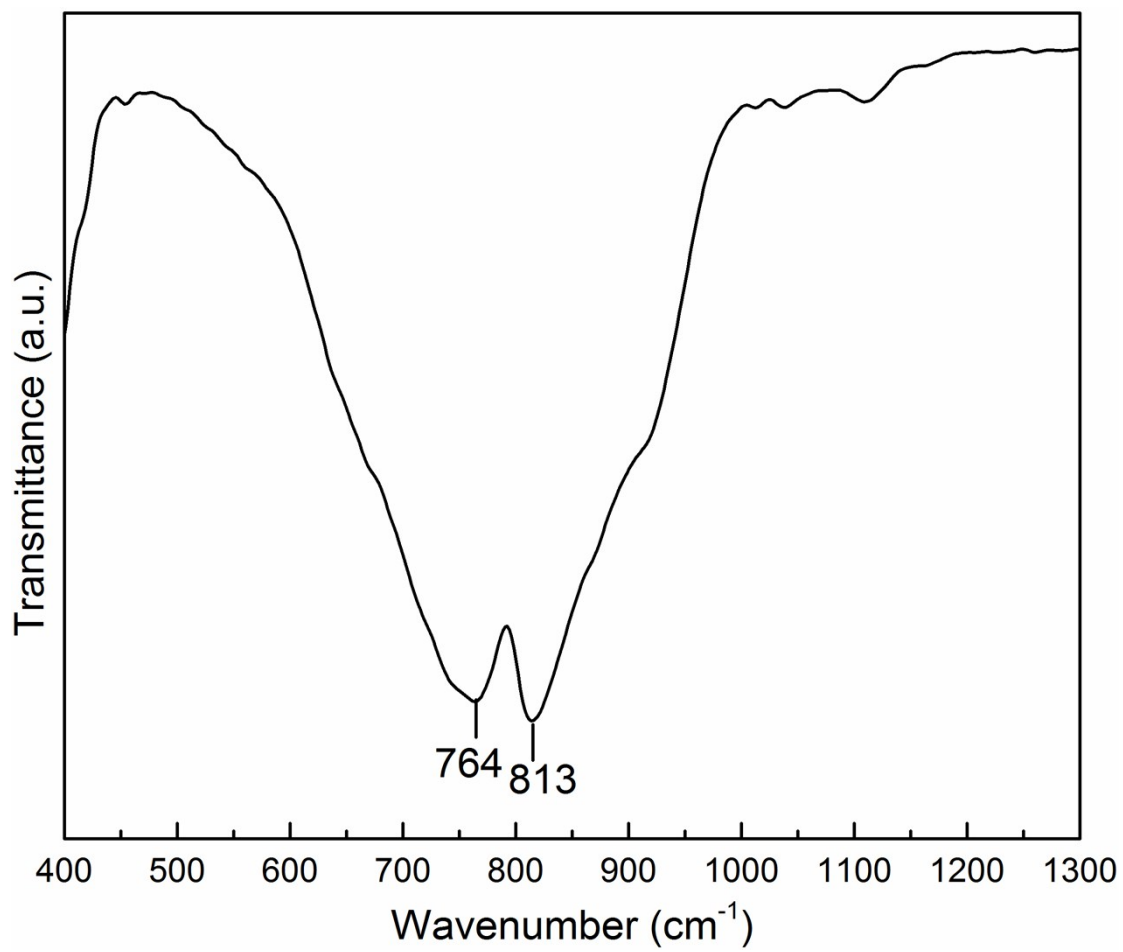


Figure S6. FTIR spectrum of the prepared WO₃ powder.

Table S2. Percentage of the area of the bands derived from deconvolution of the UV-vis spectra of W-doped TS-1 zeolite WTS(3/1), WTS(3/2) and WTS(3/3) in Figure 2a.

Sample	Peak center				Area %			
	1	2	3	4	1	2	3	4
WTS(3/1)	210	229	266	332	69.24%	3.02%	23.71%	4.03%
WTS(3/2)	210	227	265	331	68.53%	3.41%	23.83%	4.23%
WTS(3/3)	210	228	265	331	67.65%	4.15%	23.52%	4.68%

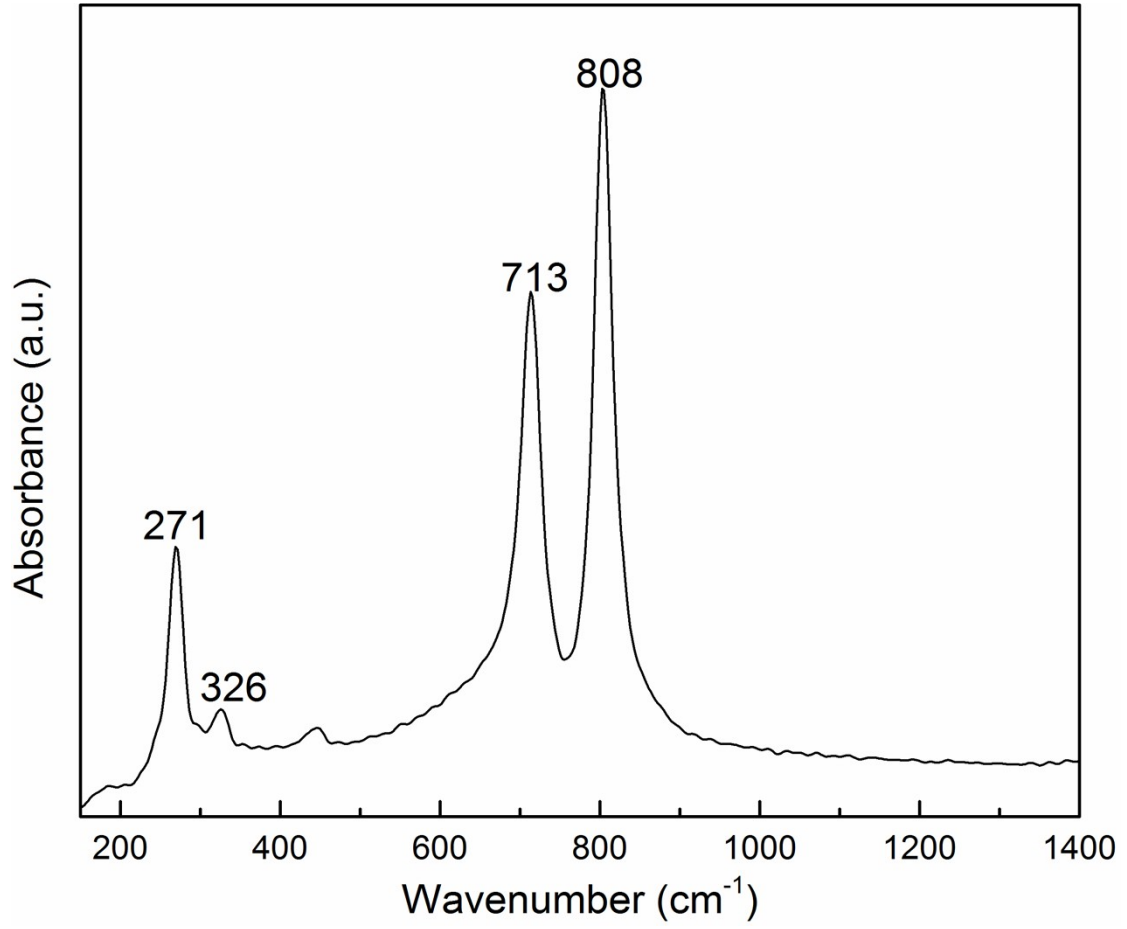


Figure S7. UV-Raman spectrum of the prepared WO₃ powder.

Table S3. TBHP conversion data for the oxidation of DBT, BT and 4,6-DMDBT.

Organosulfur compounds	Zeolite catalysts				
	WS(29)	TS(29)	WTS(3/1)	WTS(3/2)	WTS(3/3)
DBT	65.8	78.4	81.6	84.2	88.3
BT	44.4	58.1	73.9	74.4	77.1
4,6-DMDBT	56.3	72.5	79.2	82.8	83.4

Table S4. NH₃-TPD results of the prepared TS(29), WS(29) and WTS(3/3) zeolite catalysts.

Sample	Acid sites (mmol NH ₃ /g)	
	Weak	Strong
WS(29)	0.006	0.0174
TS(29)	0.0287	0.0328
WTS(3/3)	0.0272	0.0405

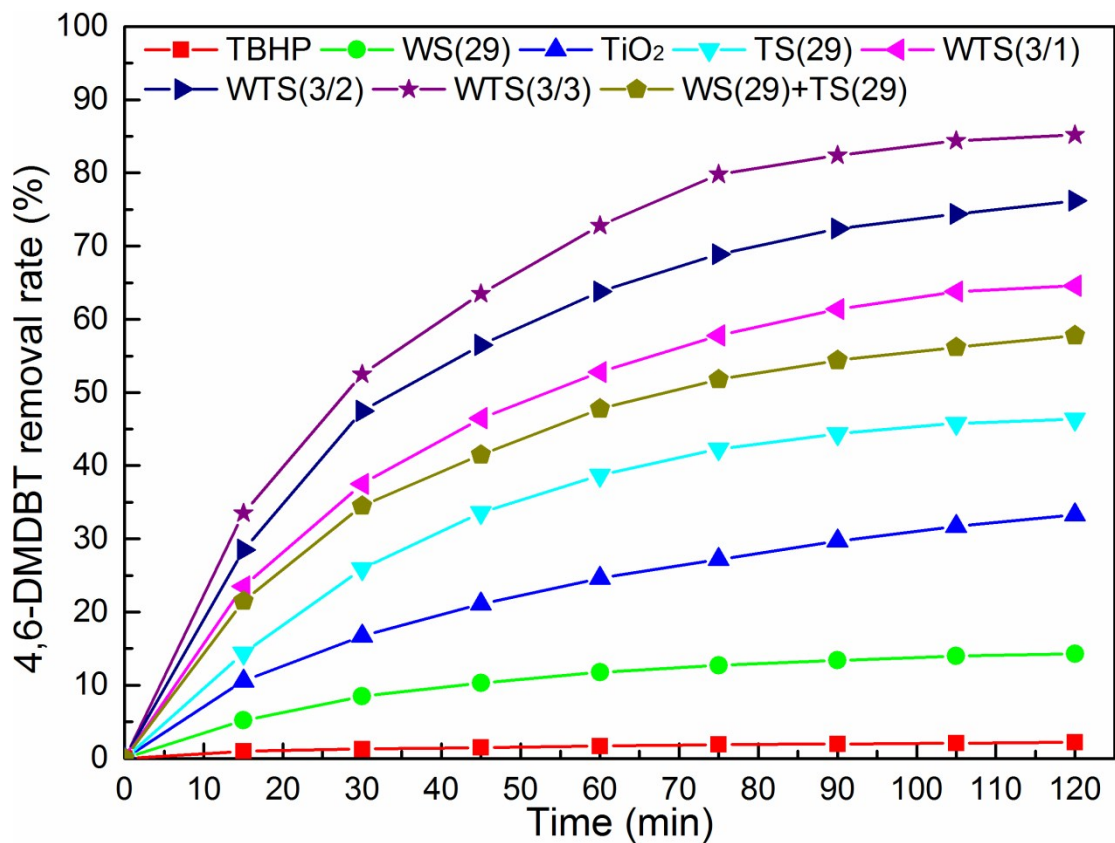


Figure S8. Oxidation of 4,6-DMDBT with TBHP alone and anatase TiO₂, WS(29), TS(29), WTS(3/1), WTS(3/2), WTS(3/3) as heterogeneous catalyst as well as TBHP as oxidant.

Table S5. Lewis and Brønsted acid sites of the prepared TS(29), WS(29) and WTS(3/3) zeolite catalysts determined by Py-IR absorbance spectra.

Sample	Brønsted acid sites ($\mu\text{mol/g}$)		Lewis acid sites ($\mu\text{mol/g}$)		LS ^a ($\mu\text{mol}/\mu\text{mol}$)	
	150 °C	350 °C	150 °C	350 °C	150 °C	350 °C
	WS(29)	118.2	14.5	59.6	18.8	5.8
TS(29)	36.1	6.4	213.2	55.9	0.4	0.1
WTS(3/3)	175.5	26.1	318.4	82.8	0.6	0.2

^a LS_W = Lewis acid amount/tungsten element amount, LS_{Ti} = Lewis acid amount/titanium element amount, LS_{W+Ti} = Lewis acid amount/(tungsten element amount + titanium element amount).

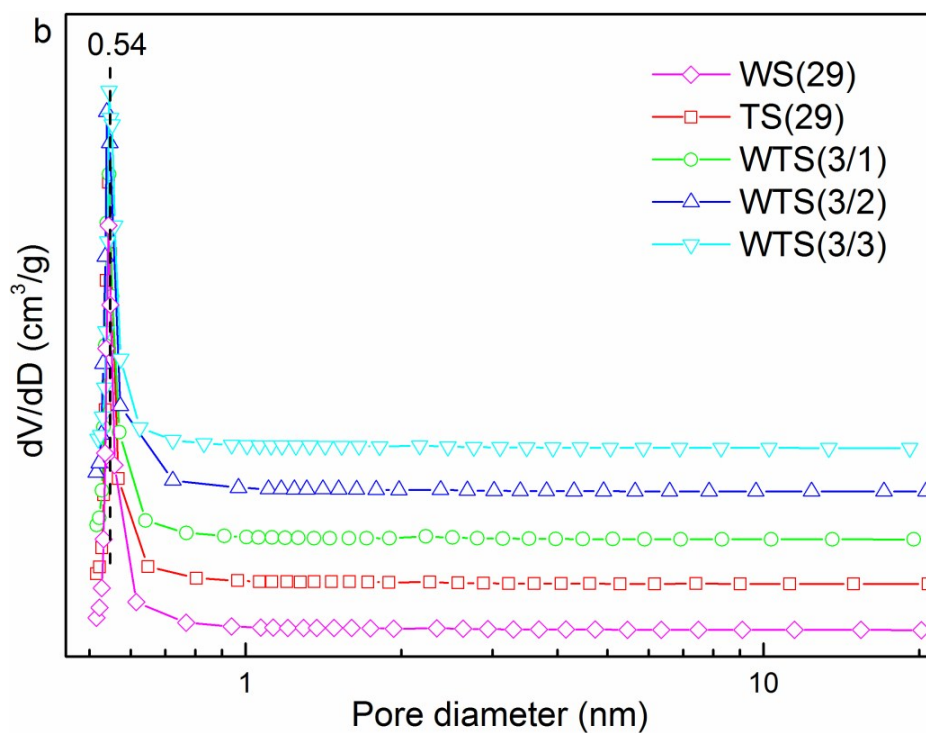
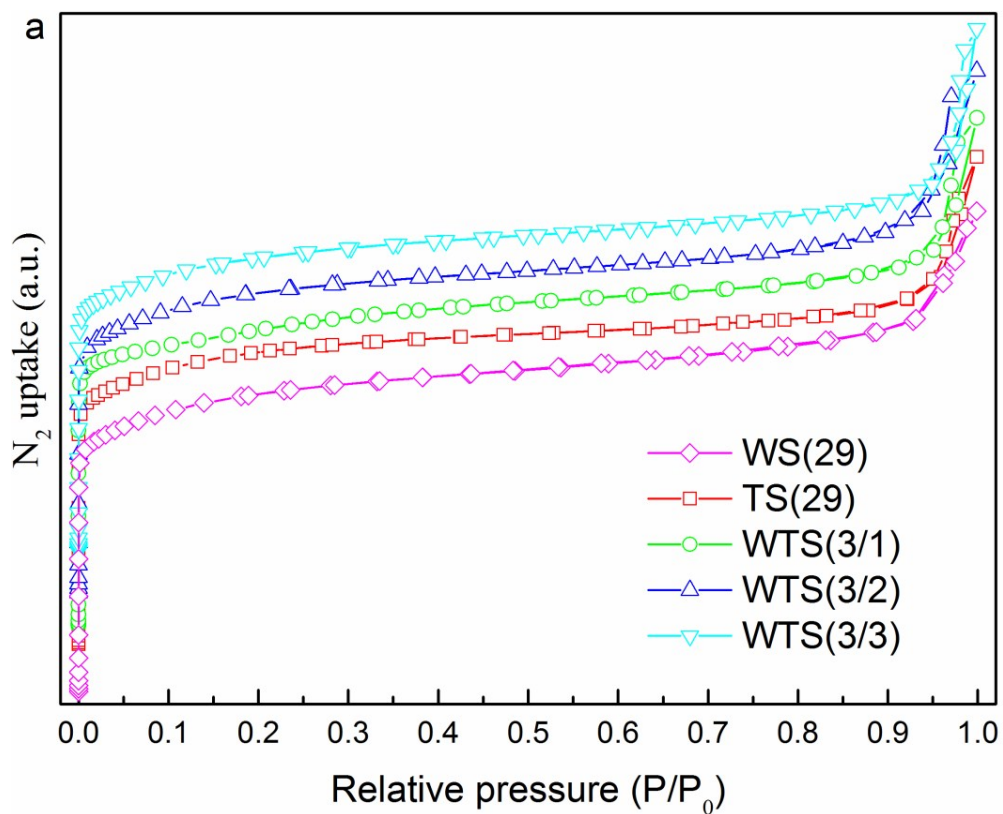


Figure S9. Nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) for the prepared W-MFI zeolite WS(29), Ti-MFI zeolite TS(29) and W-doped TS-1zeolite WTS(3/1), WTS(3/2), WTS(3/3).

Table S6. Textural parameters of the prepared W-MFI zeolite WS(29), Ti-MFI zeolite TS(29) and W-doped TS-1zeolite WTS(3/1), WTS(3/2), WTS(3/3).

Sample	Ti ^a (wt%)	W ^a (wt%)	S _{BET} ^b (m ² /g)	S _{micro} ^d (m ² /g)	S _{ext} ^e (m ² /g)	V _{tot} ^c (cm ³ /g)	V _{micro} ^d (cm ³ /g)	V _{ext} ^e (cm ³ /g)
WS(29)	/	0.19	411	382	29	0.33	0.2	0.13
TS(29)	2.51	/	413	381	32	0.34	0.2	0.14
WTS(3/1)	2.51	0.21	416	380	36	0.35	0.2	0.15
WTS(3/2)	2.51	0.50	420	381	39	0.35	0.2	0.15
WTS(3/3)	2.51	0.93	421	380	41	0.36	0.2	0.16

^a Titanium and tungsten content are measured by XRF.

^b S_{BET} represents the specific surface area.

^c V_{tot} is denoted as adsorption pore volume at P/P₀ = 0.9988.

^d S_{micro} and V_{micro} are determined using t-plot method.

^e S_{ext} = S_{BET} - S_{micro}, V_{ext} = V_{tot} - V_{micro}.

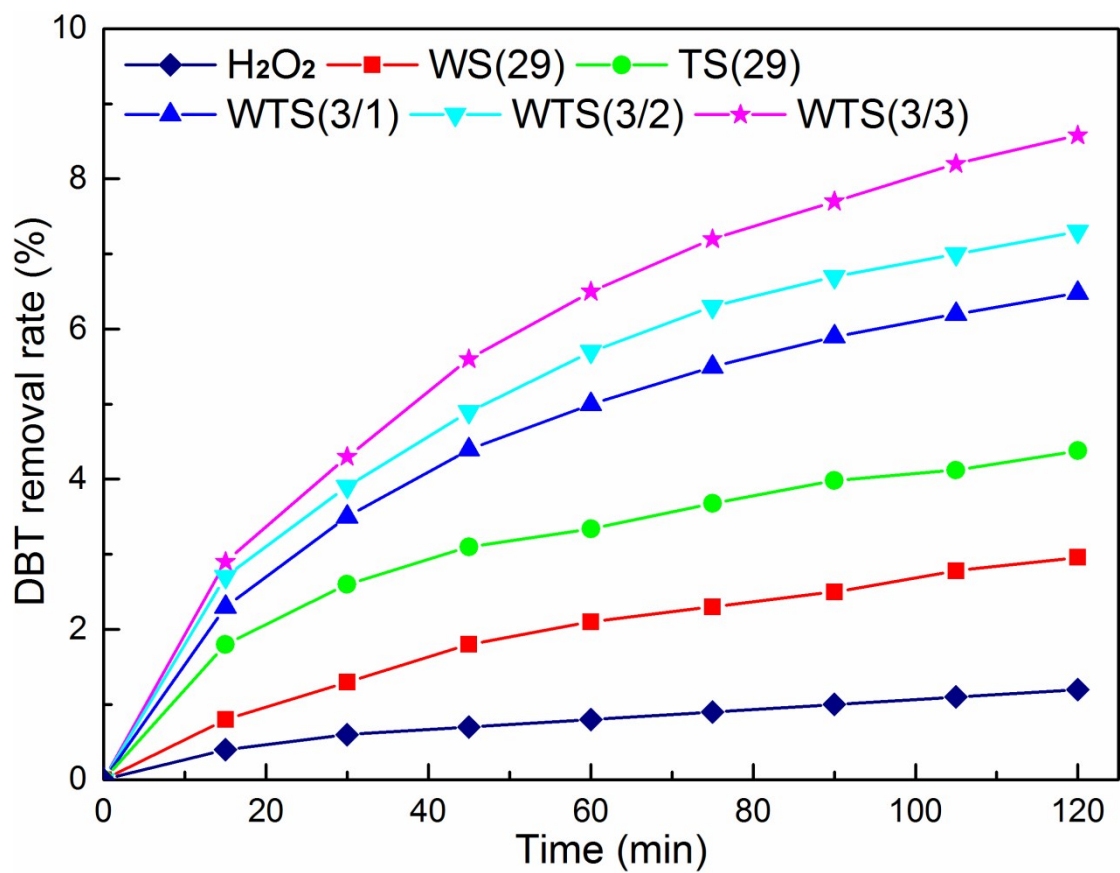
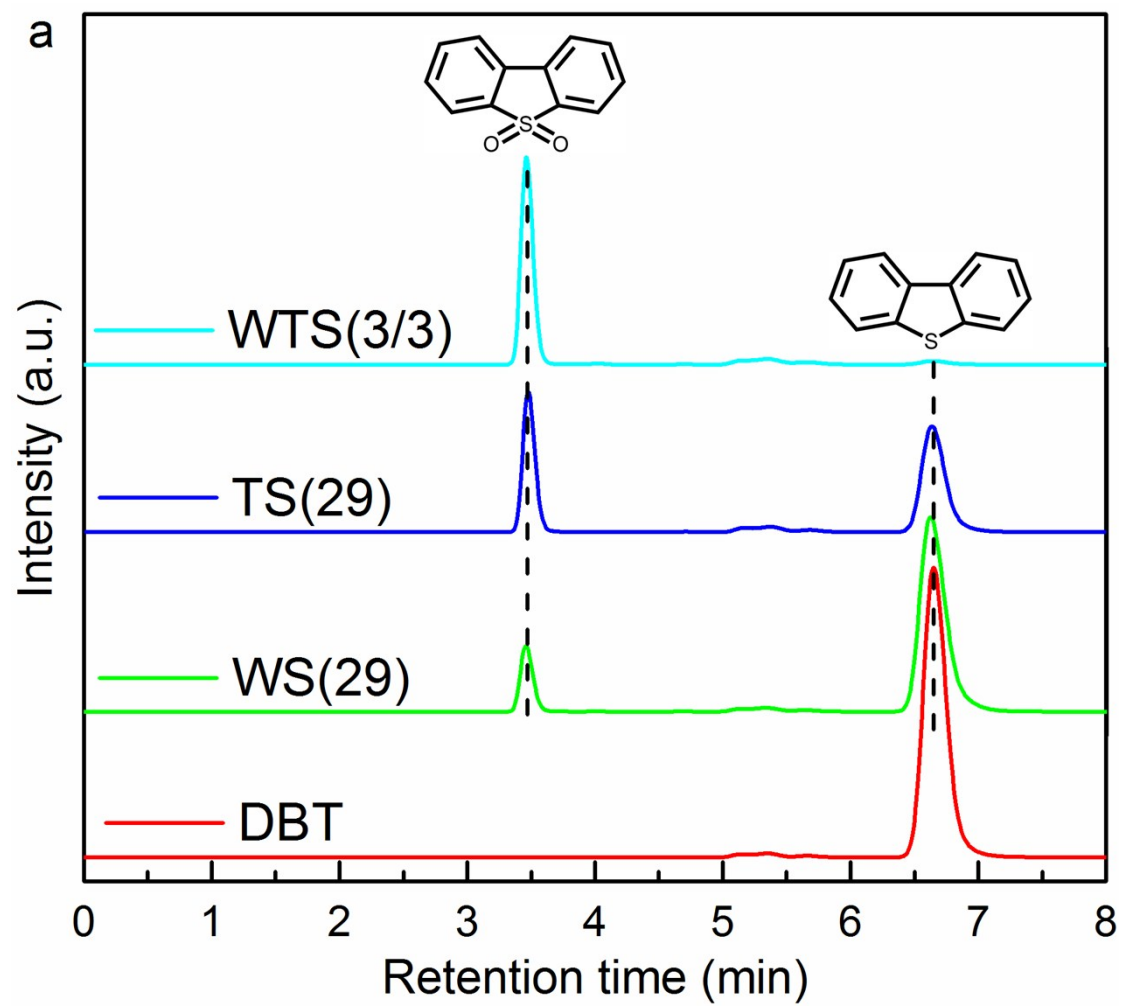
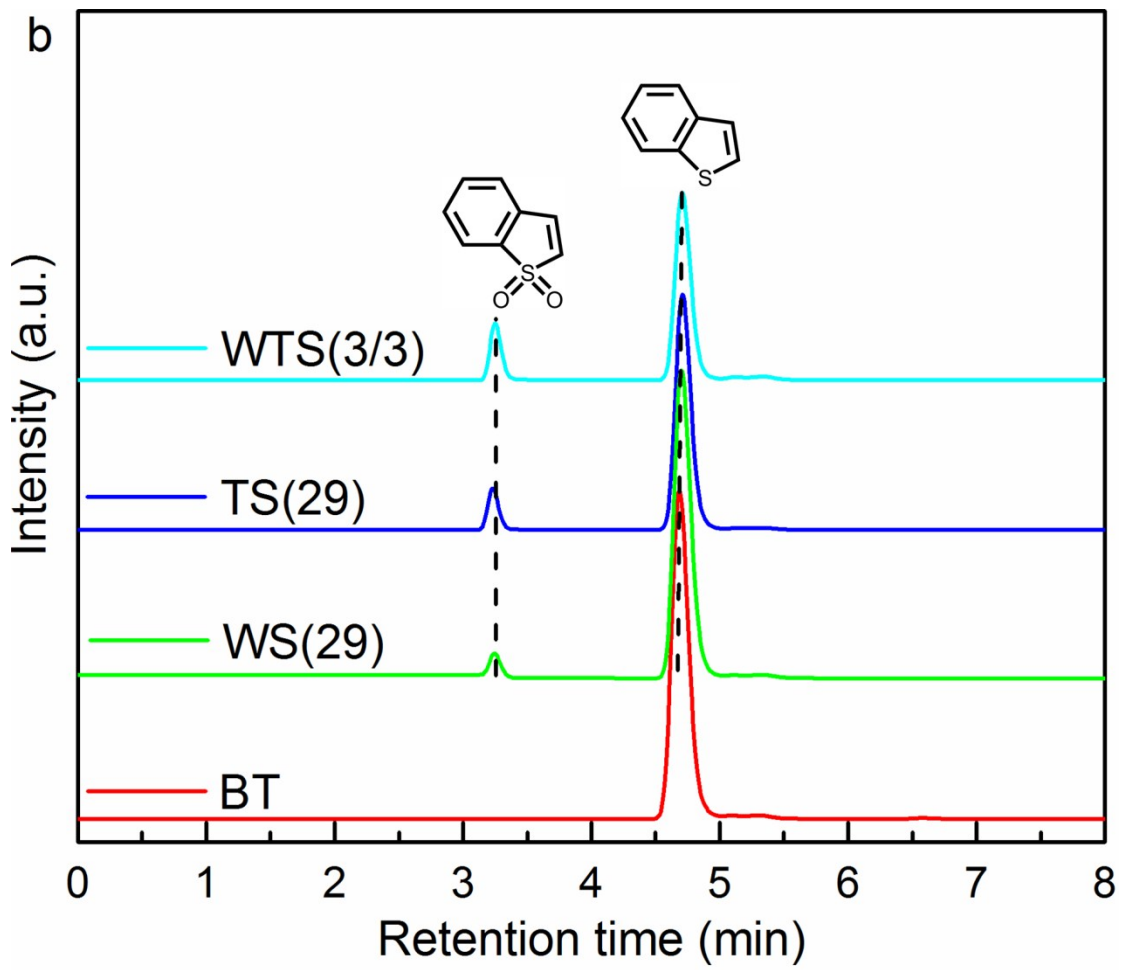


Figure S10. Oxidation of DBT with H₂O₂ alone and TS(29), WS(29), WTS(3/1), WTS(3/2) and WTS(3/3) zeolite as heterogeneous catalyst as well as H₂O₂ as oxidant.





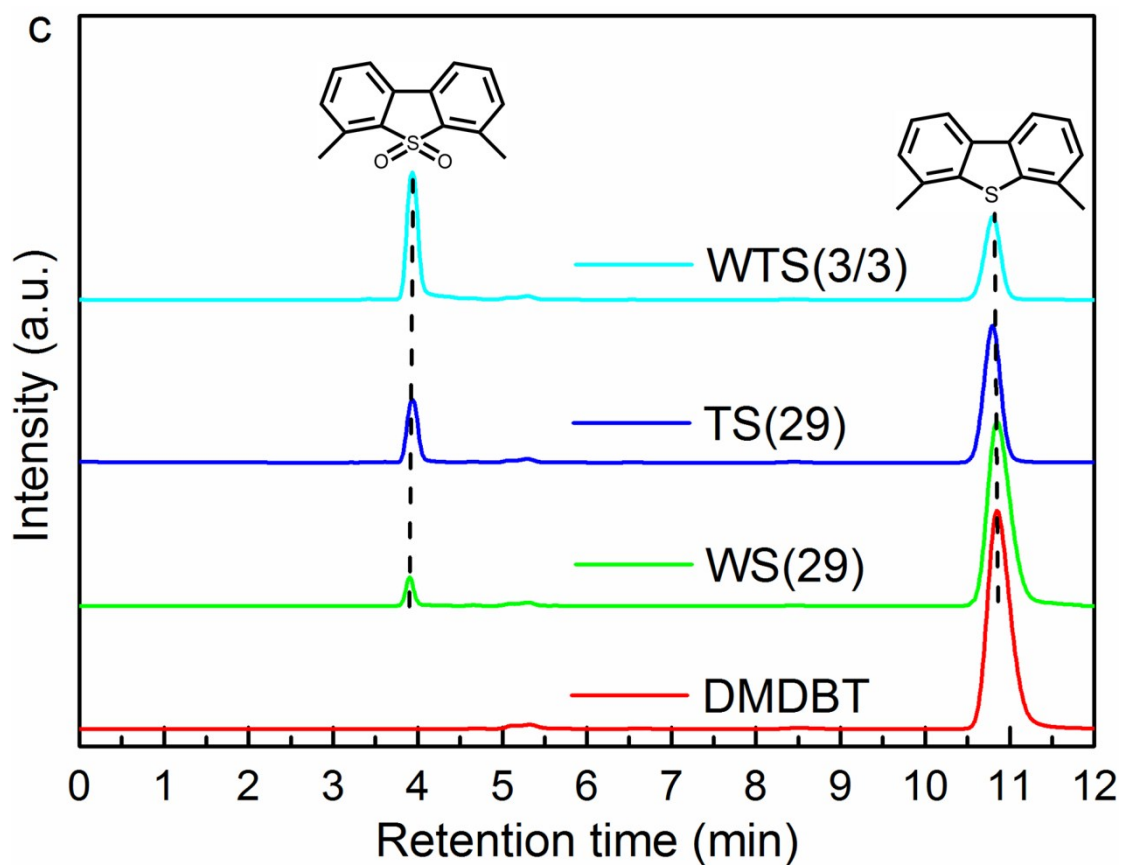


Figure S11. LC chromatograms of oxidation of DBT (a), BT (b) and 4,6-DMDBT (c) with WS(29), TS(29) and WTS(3/3) as heterogeneous catalyst. The structures annotated onto the chromatograms are identified by the molecular weight determined by GC-MS.

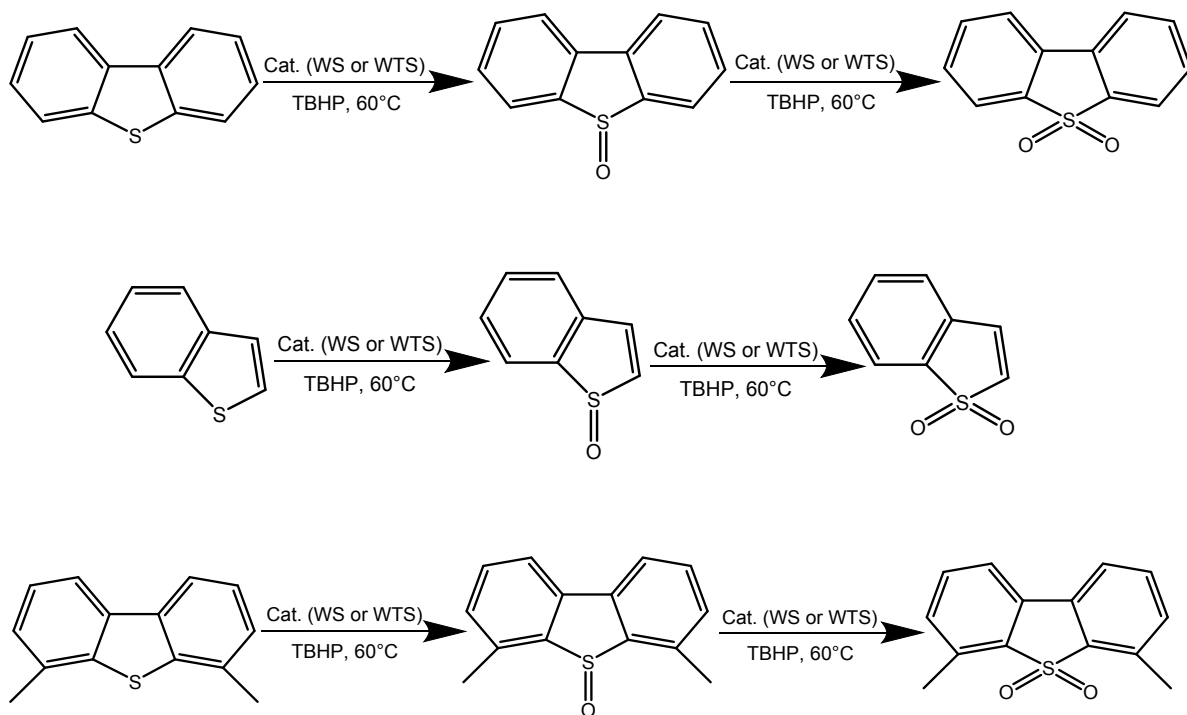


Figure S12. TBHP oxidation reactions of different S-containing organic compounds with tungsten-containing zeolite as heterogeneous catalyst.

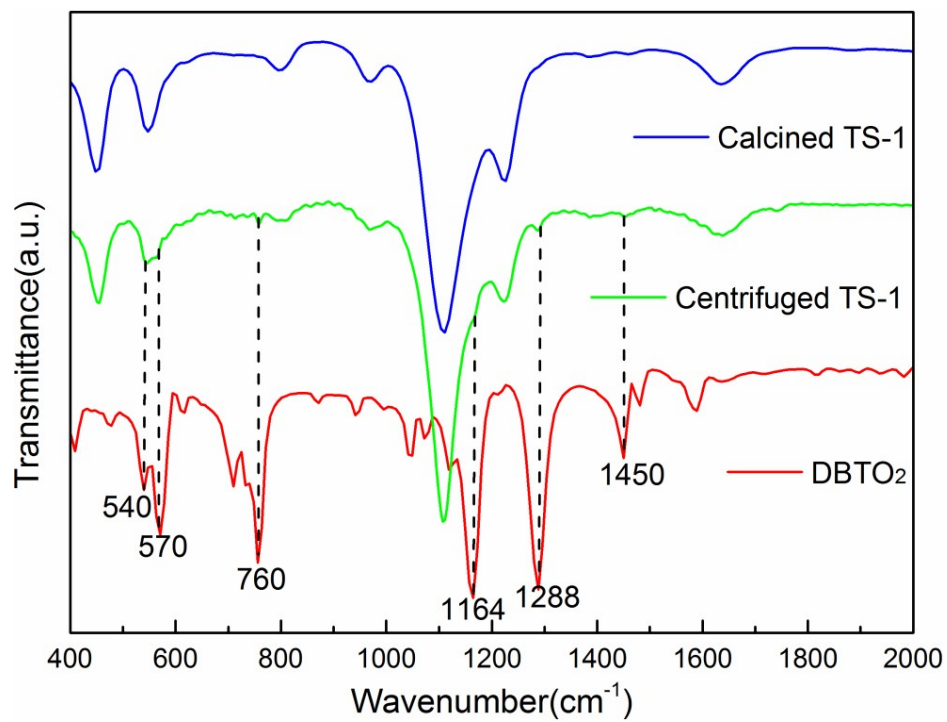


Figure S13. FTIR spectra of dibenzothiophene sulfone DBTO₂, centrifuged WTS(3/3) and calcined WTS(3/3).

Table S7 Recycle tests in the oxidation of DBT using the calcined recycled WTS(3/3) zeolite.

Runs	DBT removal rate (%)			
	30 min	60 min	90 min	120 min
1	80.2	94.1	98.1	99.8
2	79.9	93.9	98.0	99.8
3	79.6	93.7	98.0	99.7
4	79.3	93.6	97.9	99.7
5	79.1	93.4	97.9	99.7
6	78.9	93.1	97.8	99.7
7	78.7	93.0	97.8	99.7
8	78.4	92.8	97.7	99.7
9	78.2	92.6	97.6	99.6
10	78.0	92.4	97.5	99.6

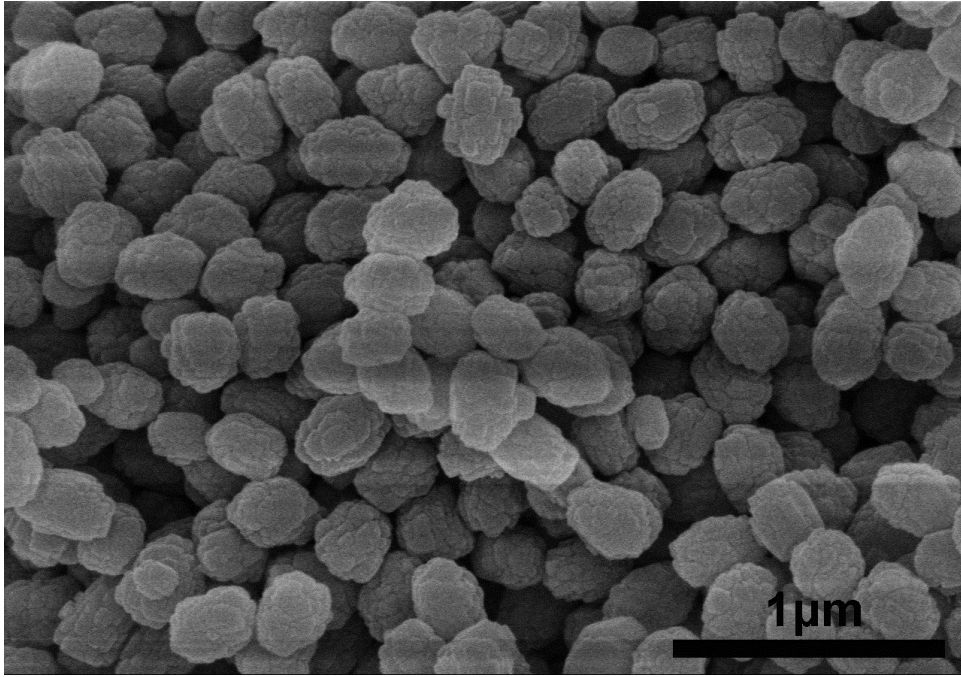


Figure S14. SEM image of the calcined recycled WTS(3/3) zeolite.

Table S8. XRF analysis of the calcined recycled WTS(3/3) zeolite.

Sample	Ti ^a (wt%)	W ^a (wt%)
WTS(3/3)	2.51	0.92

^a Titanium and tungsten content are measured by XRF.

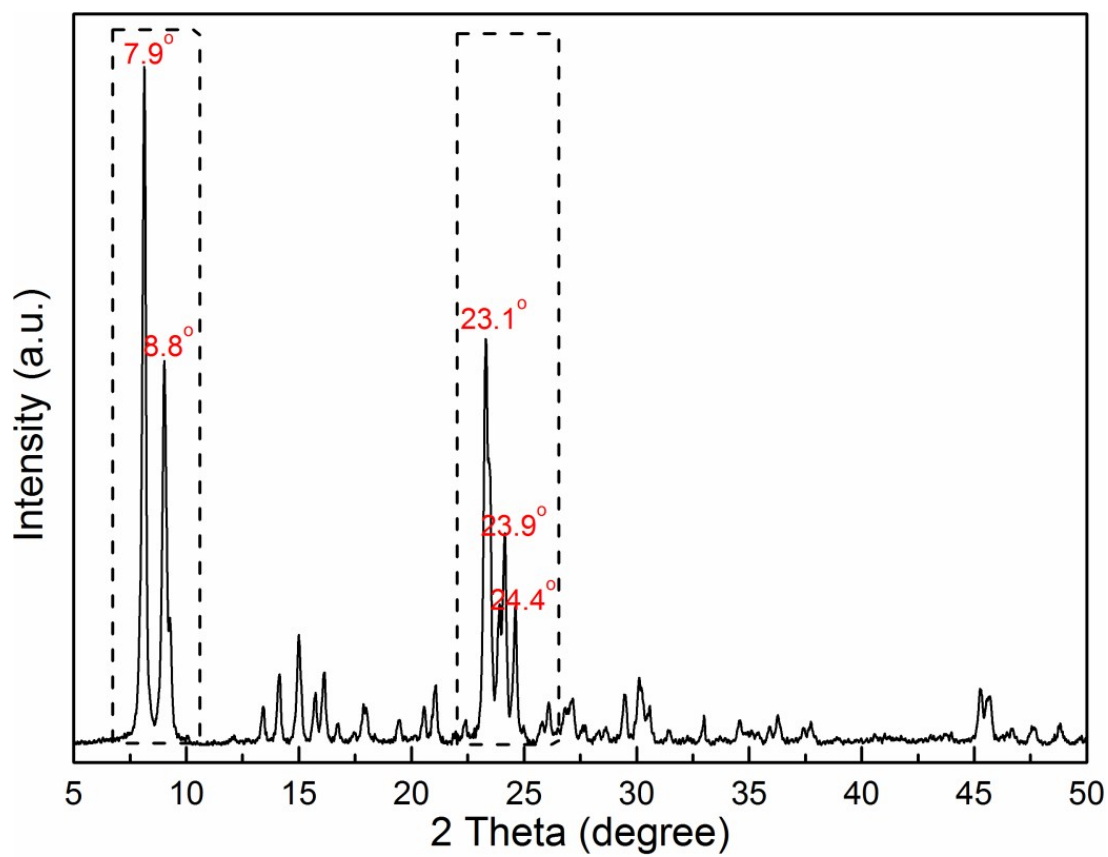


Figure S15. XRD pattern of the calcined recycled WTS(3/3) zeolite.