Supporting Information

Preparation, characterization, and catalytic performances of a pyrazine dicarboxylate-bridging rare-earth-containing polytungstoarsenate aggregate for selective oxidation of thiophenes and deep desulfurization of model fuels

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Section 1 Additional Structural Figure

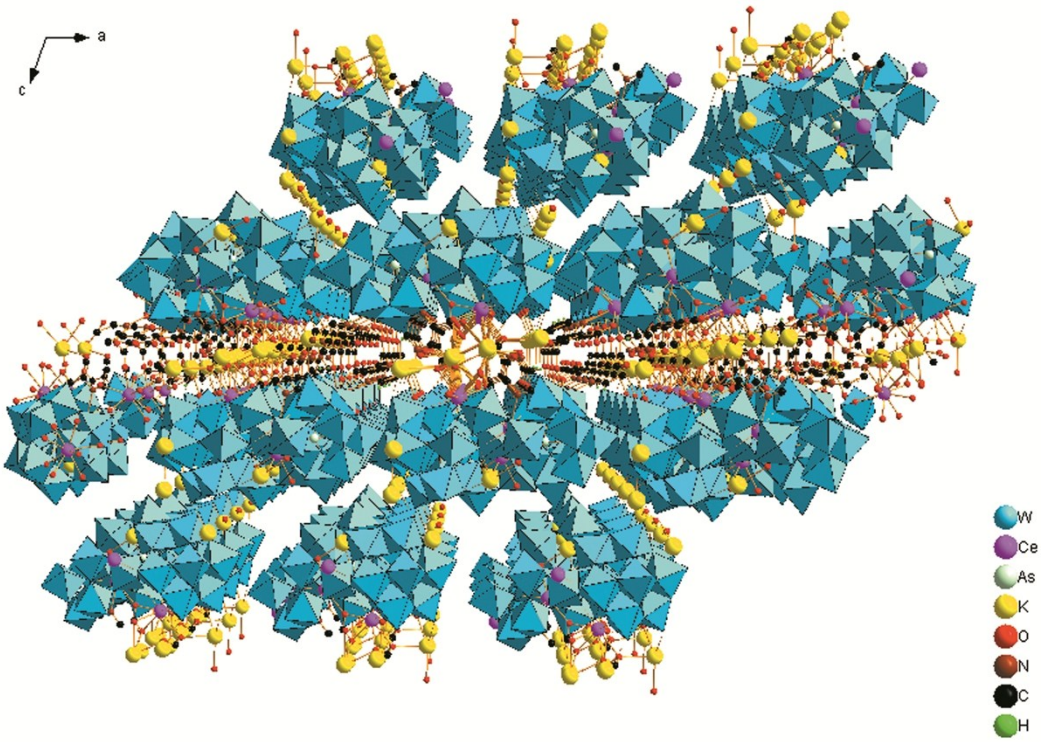


Figure S1. The 3D structure of **1**

Section 2 Experimental Section

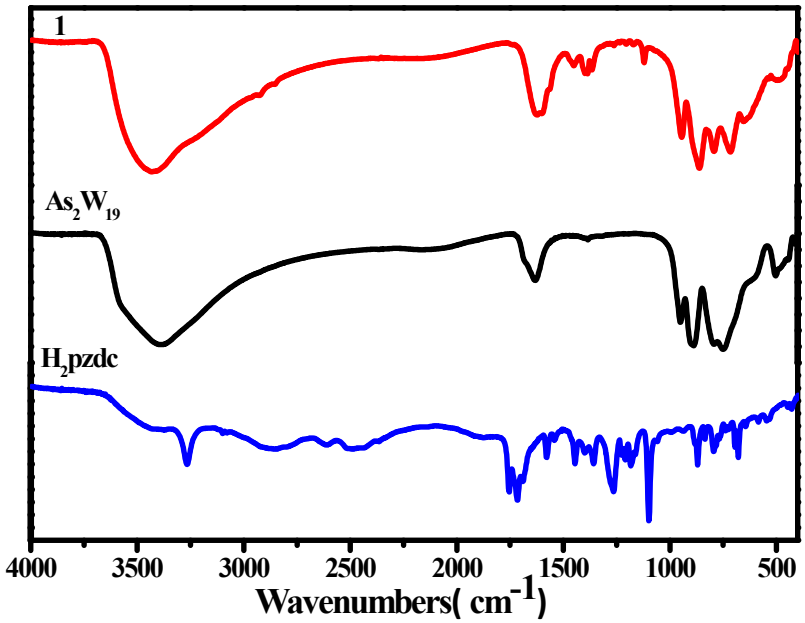


Figure S2. The IR spectra of the precursor free H_2pzdc ligand, {As_2W_{19}}, and **1**

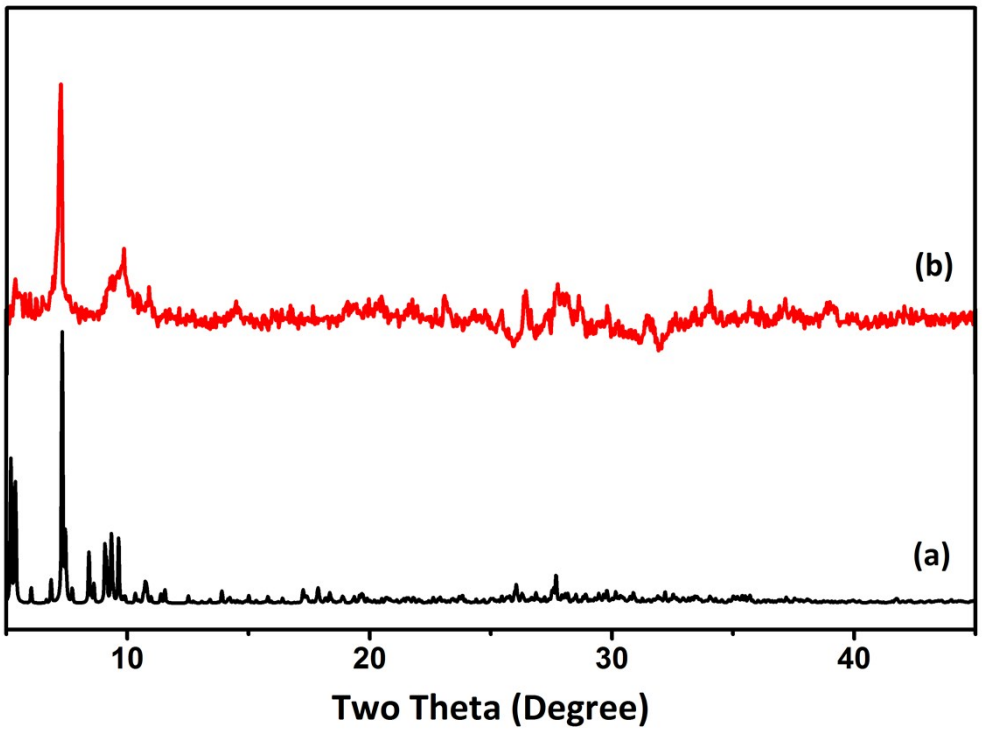


Figure S3. The experimental (a) and simulated (b) PXRD pattern of **1**

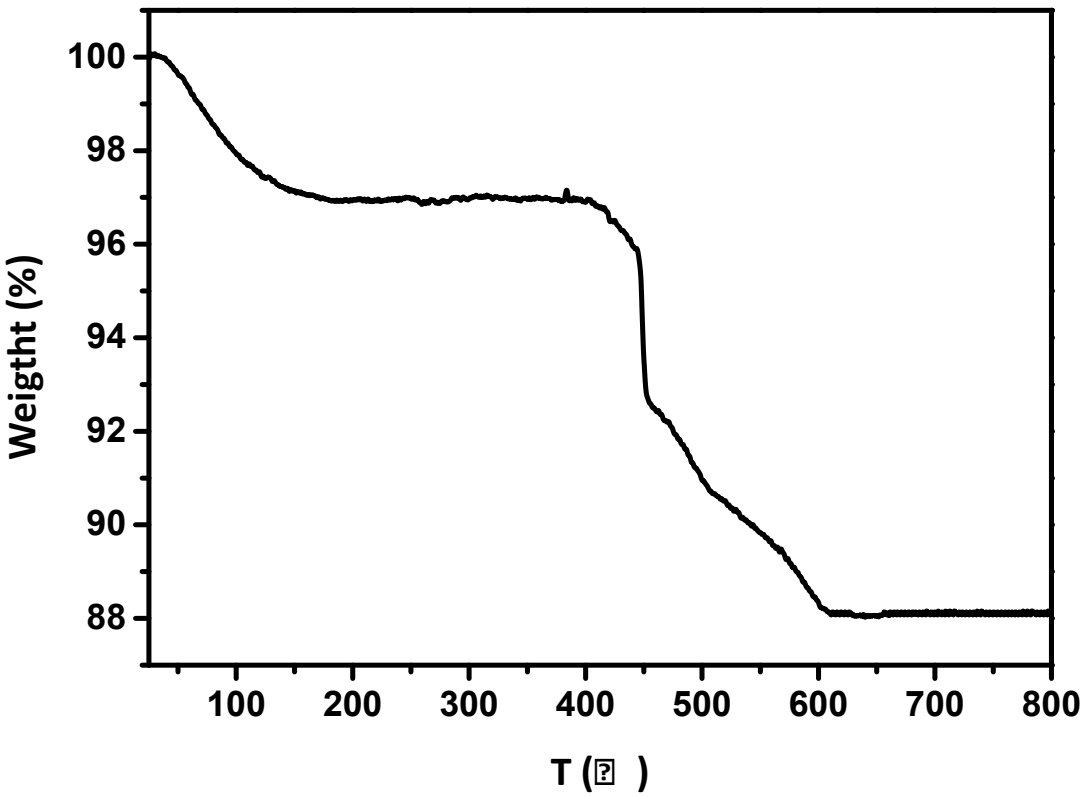


Figure S4. TG curve of **1** in a N_2 atmosphere in the range of 25–800 ºC.

The TGA curve (Figure S4) shows two steps of weight loss at the range of 25–800 °C. The first weight loss is 3.10 % (calcd 7.2 %) from 25 to 400 °C, assigned to the release of 22 lattice water molecules and 14 coordinated water molecules. The second weight loss is 8.60 % (calcd 8.2 %) at the range of 600–800 °C, which can be ascribed to the removal of 2 ligands, 3 constitutional water molecules and 1.5 As_2O_3 molecules. The first weight loss is more than the theoretical value because the samples used for thermogravimetric analyses were easy to weathering.

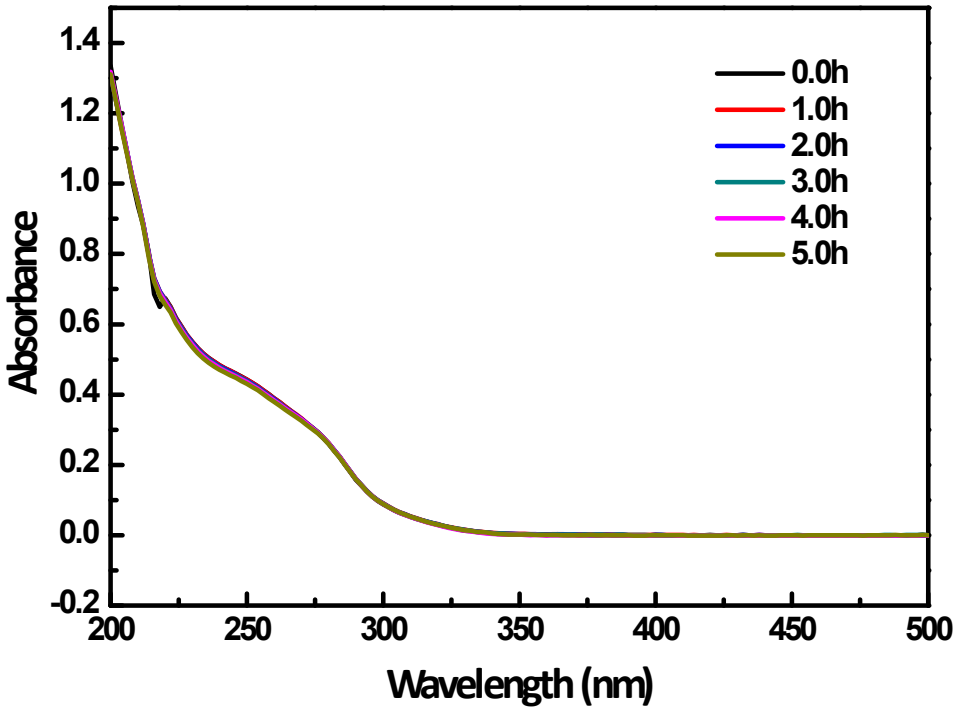


Figure S5. The UV–vis spectra of **1**

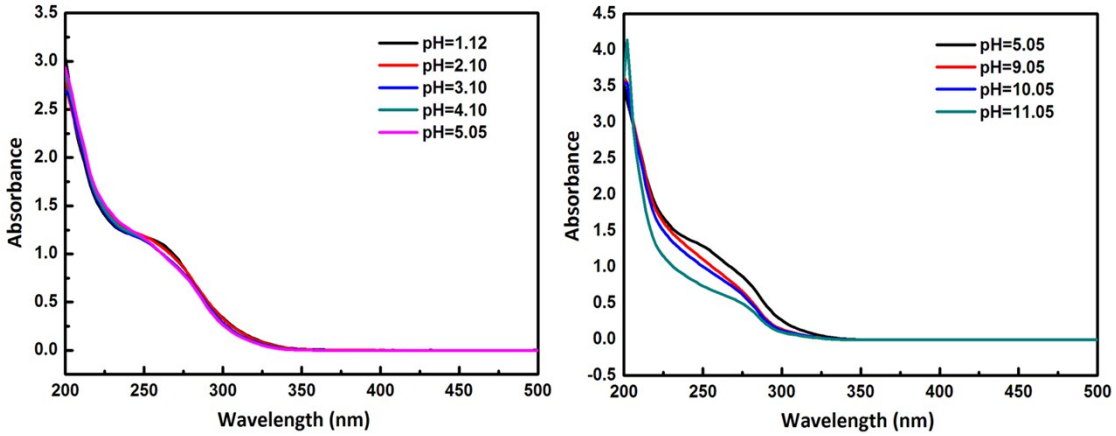


Figure S6. The UV–vis spectra of **1** at different pH values.

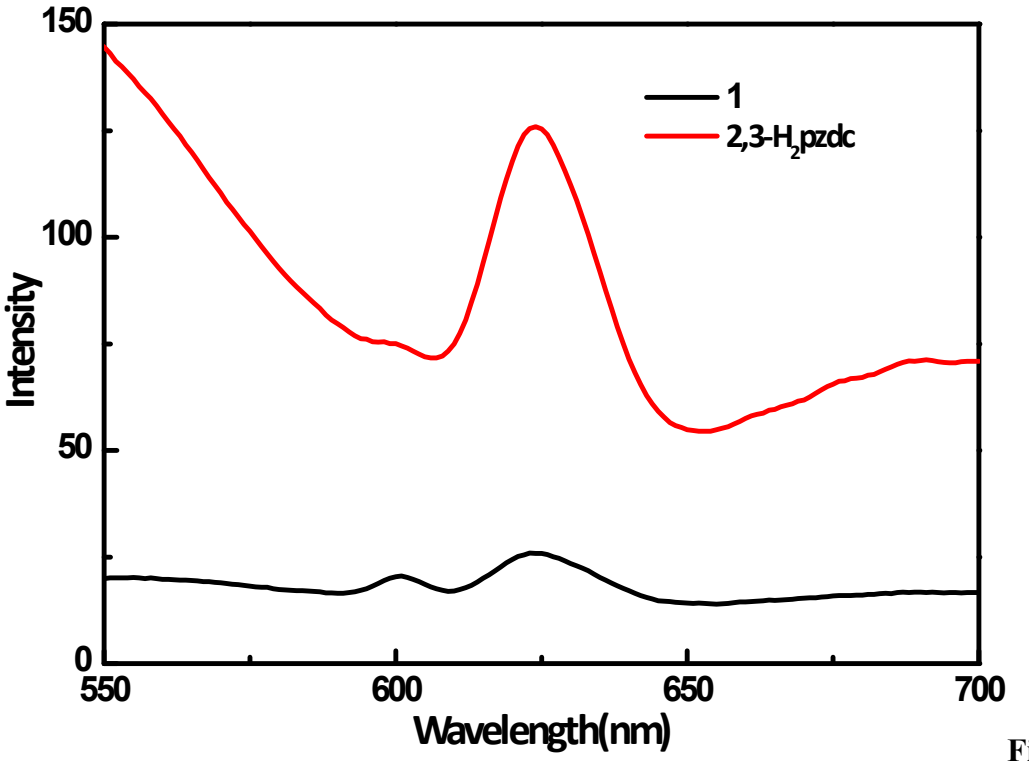


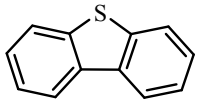
Figure S7. Solid-state emission spectra of **1** and H_2pzdc at room temperature.

Section 3 Catalytic properties

Table S1. Catalytic results for the oxidation of DBT in the presence of different POM catalysts.

catalyst	solvent	O/S	Tem. (°C)	Time (h)	Conv. (%)	Ref.
$TBA_4H_2[BW_{11}Mn(H_2O)O_{39}]\cdot H_2O$	CH_3CN	6	22-24	1	100	1
$TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$	CH_3CN/ t-BuOH	1	60	1	88	2
$[(C_{18}H_{37})_2(CH_3)_2N]_7PW_{11}O_{39}$	$C_4H_8O_2$	2.5	60	0.5	99	3
$H_6[(C_6H_4NO_2Cu(H_2O)_4)]_2[Mn_2V_{22}O_{64}]\cdot 28H_2O$	CH_2Cl_2	3	60	1.67	82	4
Fe_3O_4–PEI–$PW_{12}O_{40}$	CH_3CN	10	30	10	99	5
Fe_3O_4–SiO_2–NH_3–$PW_{12}O_{40}$	CH_3CN	10	30	10	97	5
$H_3PW_{12}O_{40}$	CH_3CN	10	30	10	99	5
$Na_{10}K_{22}[Zr_{24}O_{22}(OH)_{10}(H_2O)_2(W_2O_{10}H)_2$-$(GeW_9O_{34})_4(GeW_8O_{31})_2]\cdot 85H_2O$	CH_3CN	3	60	2	trace	6
$[Co(BBPTZ)_3][HPMo_{12}O_{40}]\cdot 24H_2O$	CH_2Cl_2	3.75	50	8	99	7
$[Co^{II}(HBBTZ)(BBTZ)_{2.5}][PMo_{12}O_{40}]$	CH_2Cl_2	3.75	50	9	98	7
$[Bmim]_3PMo_{12}O_{40}/SiO_2$	C_7H_8	3	60	1	88	8
$[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$@MCM-41-$NH^{4+}$	CH_3CN	2	40	24	100	9

Table S2. Oxidation of DBT Using Different Catalysts[a]

Entry	Catalyst	Substrate	%Conversion[b]
1	/		34
2	$K_{14}[As_2W_{19}O_{67}(H_2O)]$ (2)		20.4
3	2,3-H_2pzdc (3)		21
4	$CeCl_3 \cdot 7H_2O$ (4)		33
5	1		100
6	2+3+4		56

[a] Reaction conditions: the substrate (0.6 mmol), the catalyst corresponding to the substrate/catalyst (S/C) molar ratio of 300; the internal standard (toluene, 0.6 mmol) and H_2O_2 (1.8 mmol) were stirred in 2.0 mL of CH_3CN at room temperature for 1h. [b] Conversion values determined by GC-FID.

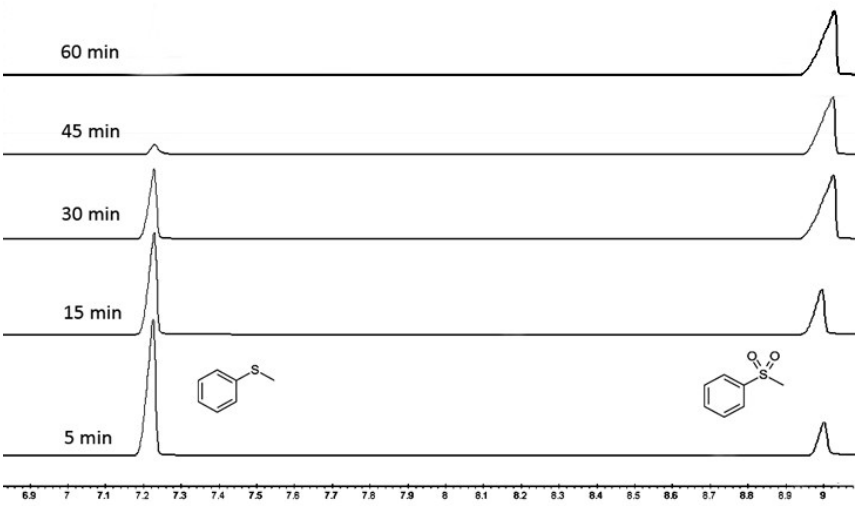


Figure. S8 Typical GC-FID chromatograms illustrating the DBT oxidation reaction profile with H_2O_2 in the presence of 1 for the S/C molar ratio of 300 at different times.

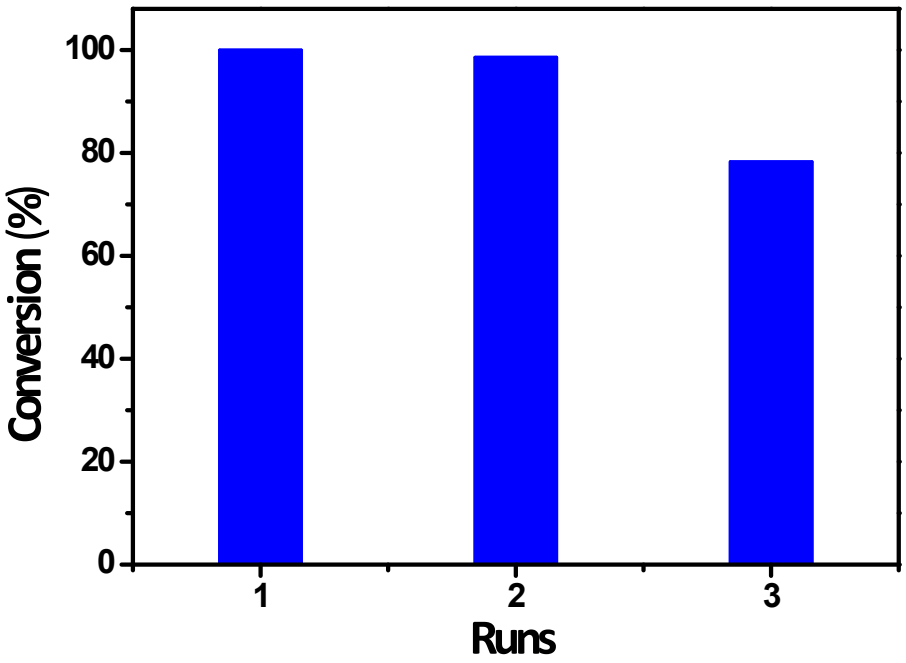


Figure S9. Reaction conditions: the substrate (0.6 mmol), the catalyst corresponding to the substrate/catalyst (S/C) molar ratio of 300; the internal standard (toluene, 0.6 mmol) and H_2O_2 (1.8 mmol) were stirred in 2.0 mL of CH_3CN at room temperature for 1h.

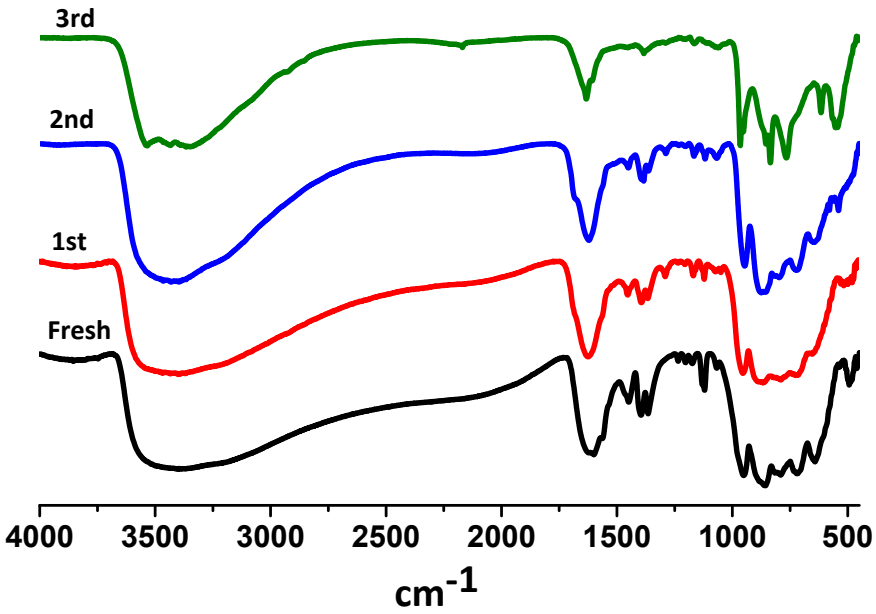


Figure S10. IR spectra of **1** before and after the recycling tests

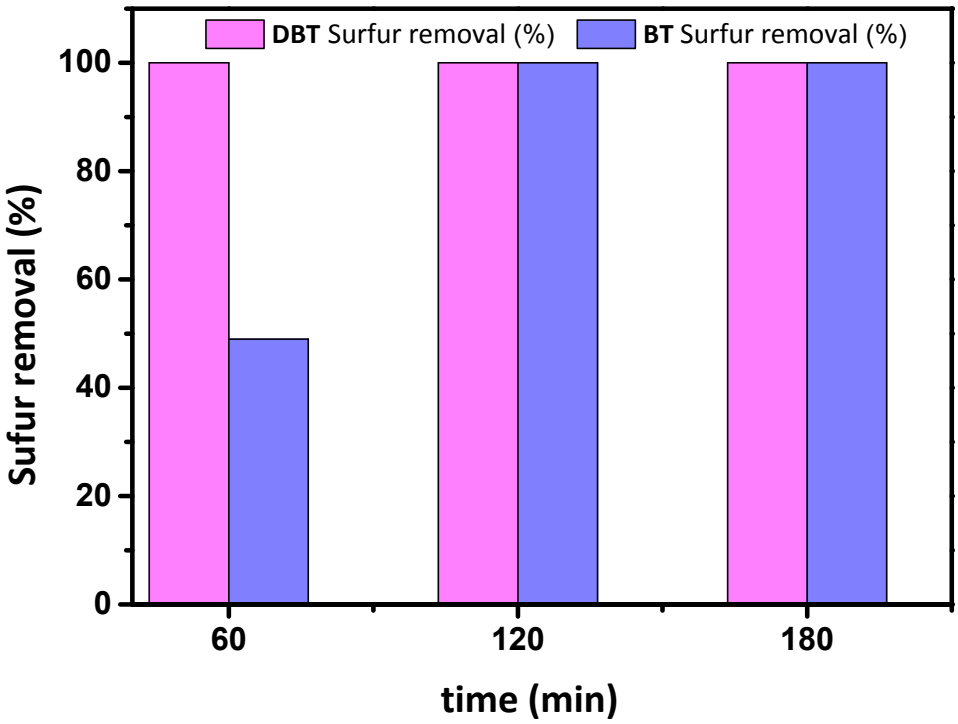


Figure S11. Reaction conditions: two substrates (0.06 mmol DBT, 0.06 mmol BT , a total of 0.12 mmol) and the catalyst were dissolved in 500 μL of CH_3CN, and the total reaction volume was completed with 1.5 mL of octane. Addition of H_2O_2 and completion of the reaction were done as indicated above.

Section 4 References

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