

Deep desulfurization upon inverse-micellar polyoxometalates and oxygen

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S1. Materials and Physical measurements

All chemicals and solvents used were AR grade or better without further purification. Dibenzothiophene (DBT, M = 184.26, 640 mg) was dissolved in decalin (250 mL) at room temperature as simulated diesel whose sulfur content was 500 ppm. A decalin solution with a series of DBT gradients was configured as the model oil. For oxidation desulfurization, thiophene, DBT, BT and 4, 6-DMDBT were prepared from the stock solution. $(\text{NH}_4)_5\text{H}_6\text{PV}_8\text{Mo}_4\text{O}_{40}$ and $(\text{CTA})\text{PMo}_4\text{V}_8$ were prepared according to Ref. [1,2] Characterization of $(\text{CTA})\text{PMo}_4\text{V}_8$ was given in Supporting Information.

The model and manufacturer of physical measurements used were detailed in the Supplementary Information. The reaction product was determined by GC-MS. The S-content of diesel and gasoline were determined build ICP-AES (ICP 6300). IR spectra (4000 - 400 cm^{-1}) were recorded in discs on a Nicolet Magna 560 IR spectrometer. ^{31}P MAS NMR measurements were obtained using a Bruker AVANCE III 400MB spectrometer at 202.5 MHz. XRD patterns of the samples were collected on a Japan Rigaku Dmax 2000 VPC X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154178$ nm). UV-vis spectra (200 - 800 nm) were recorded on a Cary 500 UV-Vis-NIR spectrophotometer. XPS patterns of the samples were collected on a micro-focused monochromatic Al $K\alpha$ X-ray source XPS (Thermo Scientific). A SU8010 scanning electron microscope determined SEM images. Using JEM-2100 instrument to record TEM micrographs. The analysis of the recovered solutions was performed using high-performance liquid chromatography (HPLC) and samples were detected by RID detector.

S2. Catalytic oxidative desulfurization for model oil and or diesel and gasoline

Catalytic oxidative desulfurization for model oil or diesel and gasoline was done according to our previous report. The oxidation of DBT-containing model oil was conducted in a glass reactor with an oxygen bubbling device like cold trap. 0.03 mmol of catalyst and 6 mL of DBT-containing model oil were added into the reactor and heated up to the desired temperature and stirred at 500 rpm. Then molecular oxygen was bubbled through the reaction solution for 10 $\text{mL}\cdot\text{min}^{-1}$. After designated reaction time, the mixture was centrifuged in 8000 rpm for 20 min to separate the insoluble catalyst and let the mixture stand for one night to precipitate needle crystals- DBTO_2 . The insoluble catalyst was washed with alcohol to remove the decalin off the surface of the catalyst. Then the solid catalyst was reused without further treatment. The content of DBT in decalin was analyzed immediately by GC.

The oxidation of diesel and gasoline was conducted as follows: 6 mL of diesel (with 1282 ppm sulfur content) or gasoline (with 996 ppm) was mixed 0.05 mmol of catalyst in a three-necked bottle which placed in oil bath for 8 h with stirring (500 rpm) at 100 °C with flowing molecular oxygen at 10 mL/min. The oxidized oil was cooled to room temperature and centrifuged in 8000 rpm for 20 min to separate the insoluble catalyst. The separated liquid was filtered using Böchner funnel containing 0.3 g column-layer chromatographic silica gel to adsorb oxidative products.

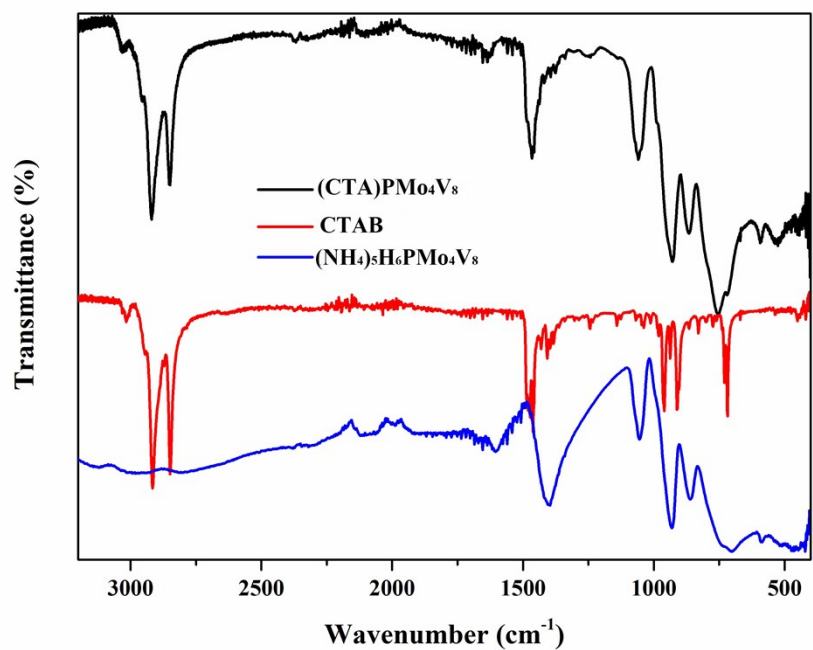


Fig. S1 The IR spectrum of (CTA)PMo₄V₈, CTAB and (NH₄)₅H₆PMo₄V₈

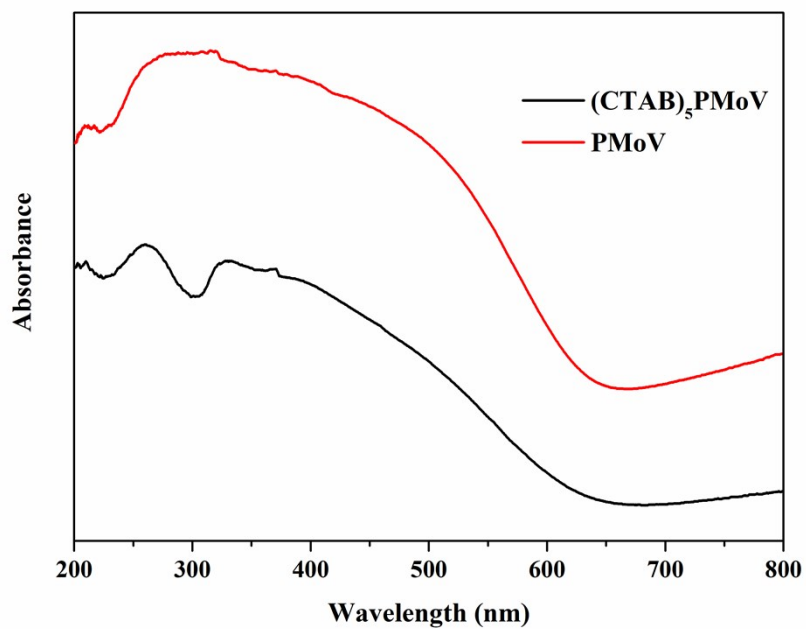


Fig. S2 The DR-UV-Vis spectra of PMoV and (CTAB)₅PMoV

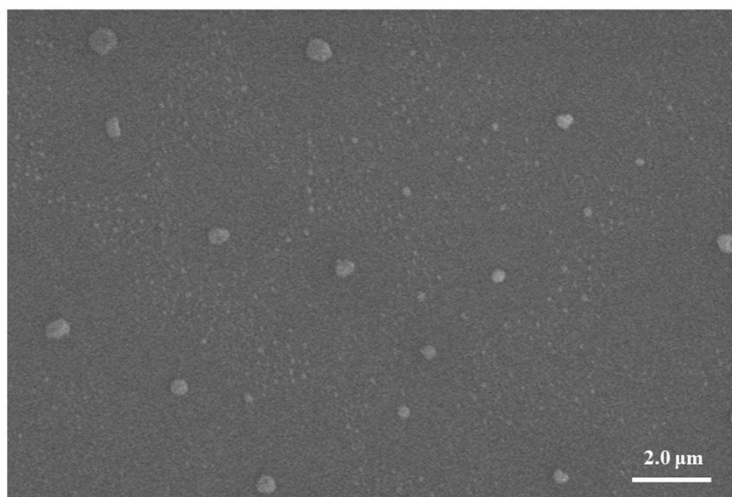


Fig. S3 The SEM image of (CTA)PMo₄V₈.

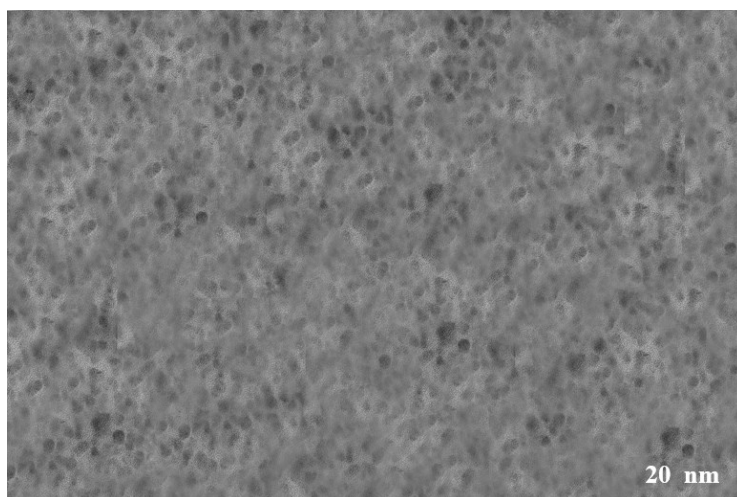


Fig. S4 The TEM images of (CTA)PMo₄V₈

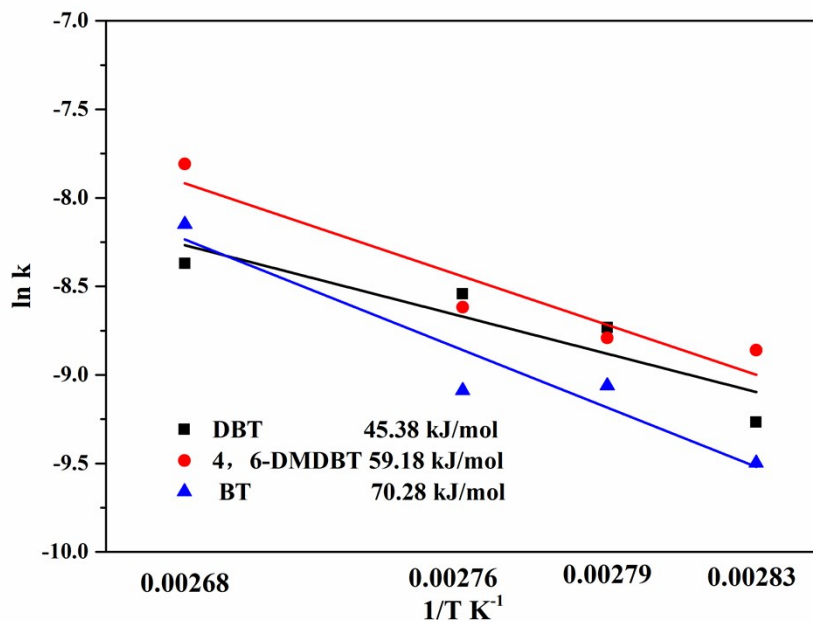


Fig. S5 Arrhenius activation energies for sulfur-containing compound oxidation with Anderson catalyst (CTA) PMo_4V_8 using dioxygen as the oxidant. Conditions: (CTA) PMo_4V_8 (0.05 mmol), sulfur-containing compound (S: 500 ppm) in 6 mL decalin, reaction temperature 80, 85, 90 and 100 °C, oxidant O_2 .

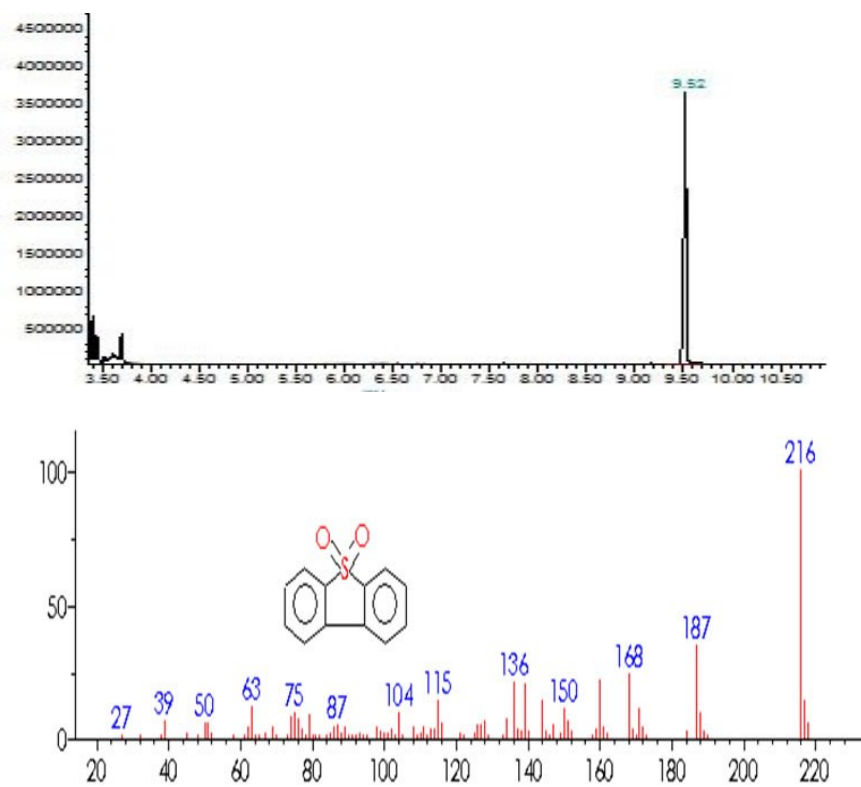


Fig. S6 GC-MS spectrum of the reaction product (dibenzothiophene sulfone)

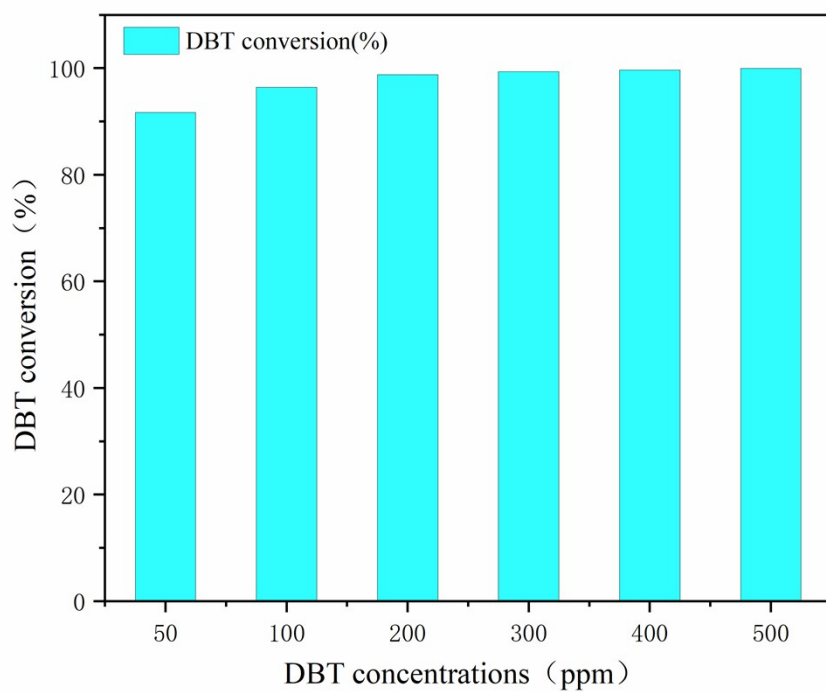


Fig. S7 The influence of DBT concentrations on the catalytic activity. Reaction conditions: DBT (500 ppm, 6 mL decalin) (CTA)PMo₄V₈ (0.05 mmol) at 100 °C with O₂, 5 h

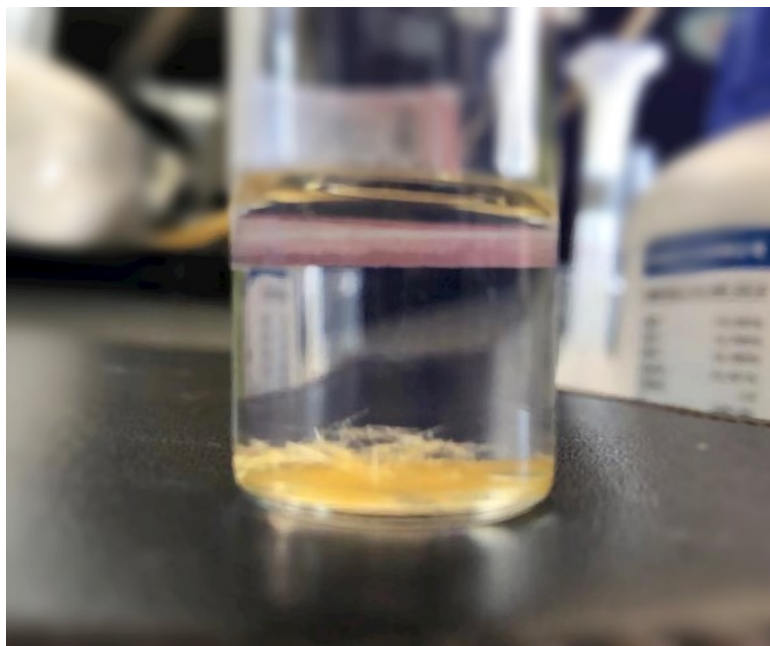
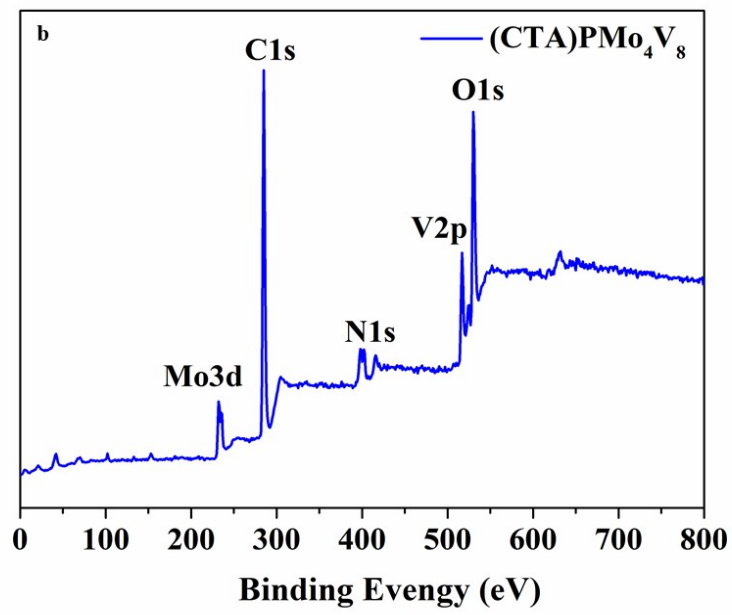
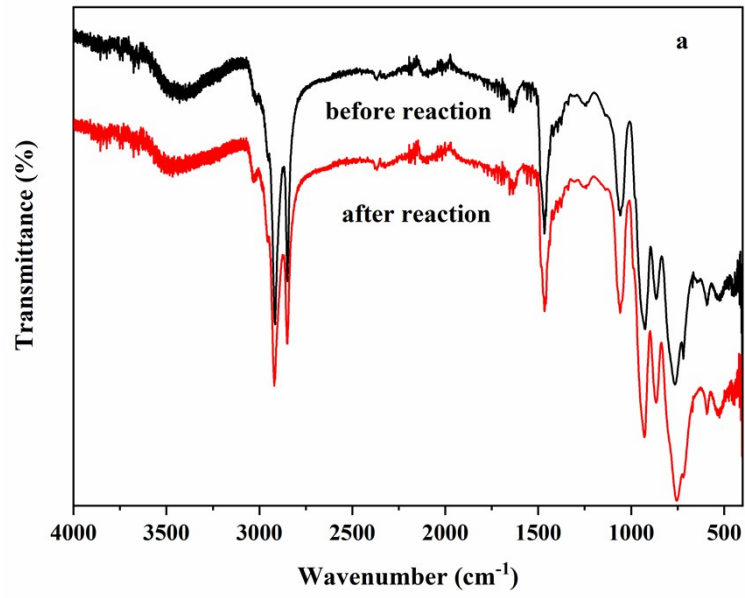


Fig. S8 The crystal of the catalytic product DBTO_2



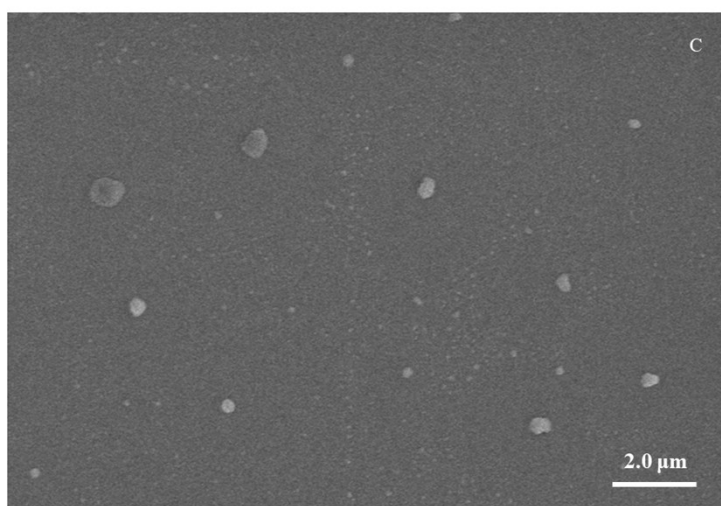


Fig. S9 The stability of (CTA)PMo₄V₈ was determined by IR(a), XPS(b) and SEM(c)

Table S1 The desulfurization upon various POMs using oxygen or air as oxidant

Catalyst	Usage (mg)	Substrate	Temperature	Reaction time	conversion	Ref.
			(°C)	(h)	(%)	
$[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$	33	DBT	60	4	100	3
$[\text{C}_8\text{H}_{17}\text{N}(\text{CH}_3)_3]_3\text{H}_3\text{V}_{10}\text{O}_{28}$	40	DBT	90	7	100	4
$[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2]_5[\text{IMo}_6\text{O}_{24}]$	39	DBT, BT, 4, 6-DMDBT	80	8, 12, 8	92, 100, 92	5
$[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2]_3\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}$	11	DBT, 4, 6-DMDBT, BT	80	5, 7, 12	100, 100, 65	6
$[\text{C}_8\text{H}_{17}\text{N}(\text{CH}_3)_3]_3\text{HIV}_9\text{O}_{28}$	40	DBT, 4, 6-DMDBT	90	6, 7	100	7
$[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]_5[\text{PMo}_{10}\text{V}_2\text{O}_{38}(\text{O}_2)_2]$	191	DBT	70	4	98	8
$[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]_7\text{PW}_{10}\text{Ti}_2\text{O}_{38}(\text{O}_2)_2$	242	DBT	90	6	100	9
$[\text{Cu}_2(\text{BTC})_{4/3}(\text{H}_2\text{O})_2]_6[\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$	44	DBT	80	1.5	100	10
$(\text{NH}_4)_3\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}$	20	DBT	60	1	99	11
$\text{H}_8\text{PV}_5\text{Mo}_7\text{O}_{40}$	910	BT	120	6	99	12
$\text{Na}_3\text{H}_6\text{CrMo}_6\text{O}_{24}$	20	DBT, 4, 6-DMDBT, BT	60	2, 3, 4	100, 100, 90	13
$\text{Na}_3\text{H}_6\text{FeMo}_6\text{O}_{24}$	20	DBT, 4, 6-DMDBT, BT	60	3, 3, 4	99, 99, 95	14
$(\text{NH}_4)_5\text{H}_6\text{PV}_8\text{Mo}_4\text{O}_{40}$	20	DBT, 4, 6-DMDBT, BT, T	100	6, 6, 11, 12	100, 100, 100, 97	15
POM@MOF-199@LZSM-5(PMZ)	150	DBT, BT	60	2	100, <80	16
$\text{PMo}_6\text{W}_6\text{O}_{40}$ @MOF-199@MCM-41	200	DBT	85	3	98.5	17

SRL-POM@MOF-199@MCM-41	150	DBT	60	2	100	18
Metal-POM@MOF-199@MCM-41	200	DBT	80	3	99.1	19
S/D/C-POM@MOF@MCM-41	150	DBT, 4, 6-DMDBT, BT	50	1.5	100, 70, 92	20
Cs-POM@MOF-199@MCM-41	200	DBT	80	5	99.6	21
PV ₈ Mo ₄ O ₄₀ @iPAF-1	12	DBT, 4, 6-DMDBT	80	5	100, 100	22
[C ₈ mim] ₃ H ₃ V ₁₀ O ₂₈ /g-BN*	80	DBT, 4-MDBT, 4, 6-DMDBT	120	4, 5, 5	99.8, 99.5, 95.3	23
CNTs@PDDA@Mo ₁₆ V ₂	100	DBT	60	3	99.4	24
CNC@PIL@POM*	20	DBT, 4, 6-DMDBT, BT	100	6, 7, 9	100	25
[(C ₈ H ₁₇) ₃ NCH ₃] ₃ PMo ₁₂ O ₄₀ /γ-MMS*	25	DBT, 4-MDBT	120	5, 7	100	26
H ₄ PMo ₁₁ V ₁ O ₄₀	12	DBT	100	6	17.3	This work

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