

Supporting Information

Polyoxovanadate-Based Cyclomatrix Polyphosphazene Microspheres as Efficient Heterogeneous Catalysts for the Selective Oxidation and Desulfurization of Sulfides

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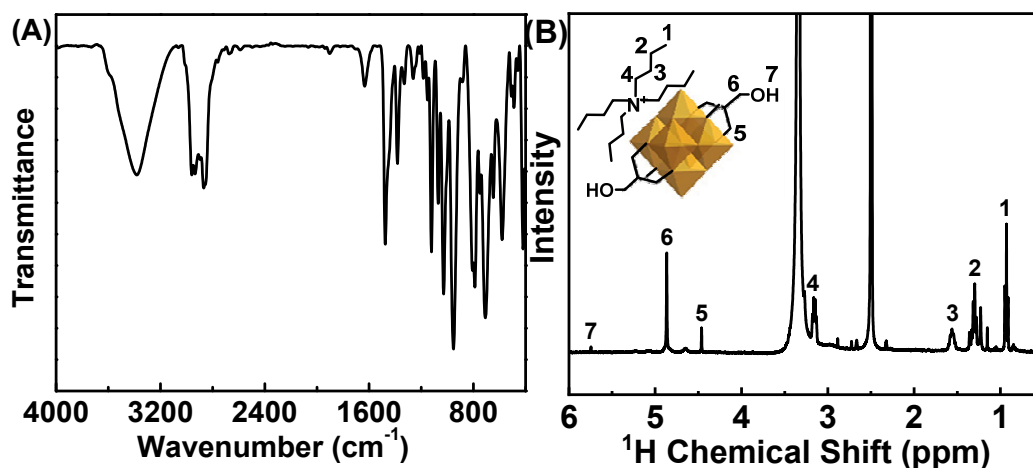


Figure S1. FT-IR spectrum (A) and ^1H NMR spectrum (B) of $\text{V}_6\text{O}_{13}\text{-OH}$ in $\text{DMSO-}d_6$.

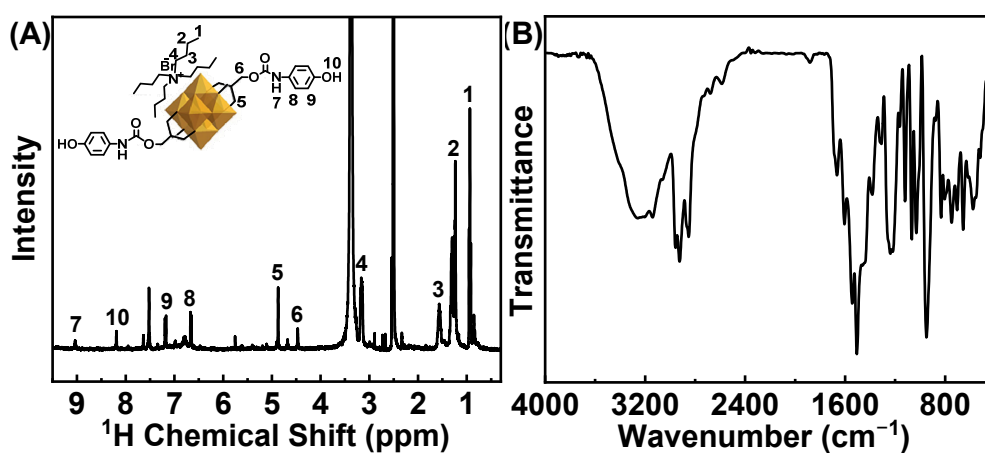


Figure S2. ^1H NMR spectrum (A) in $\text{DMSO-}d_6$ and FT-IR spectrum (B) of $\text{V}_6\text{O}_{13}\text{-PhOH}$.

TGA of HCCP-V

The calculation of the proportion of V_6 in HCCP-V: The mass of the sample put into the crucible is 6.032 mg, and the mass residual rate is 42.52% at 900 °C. Assuming that the final residual P_2O_5 and V_2O_5 of the sample are x mmol and y mmol respectively, the following equation can be obtained:

$$142x + 182y = 2.565$$

$$2 * 135x/3 + 1532y/3 = 6.032$$

Solving for $x = 0.003777$, $y = 0.01115$

P_3N_3 is 0.002518 mmol, $\text{V}_6\text{O}_{13}\text{-PhOH}$ is 0.003717 mmol

P_3N_3 : $\text{V}_6\text{O}_{13}\text{-PhOH}$ = 1: 1.476

Then the weight percentage of V_6 in **HCCP-V** is 18.85%.

SEM of HCCP-V

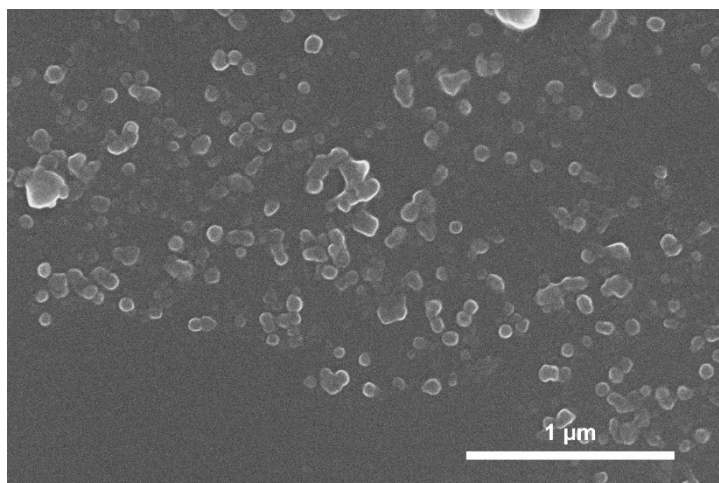


Figure S3. SEM image of **HCCP-V** dispersed in EtOH.

The HPLC standard curve of MPSO

Prepare MPSO solutions of different concentrations, 0.5 mM, 1 mM, 2 mM, 3 mM, 4 mM and 5 mM, using high performance liquid chromatography under the same mobile phase conditions as the test environment (acetonitrile: H_2O = 7:3, 10 μL) to give the standard curve.

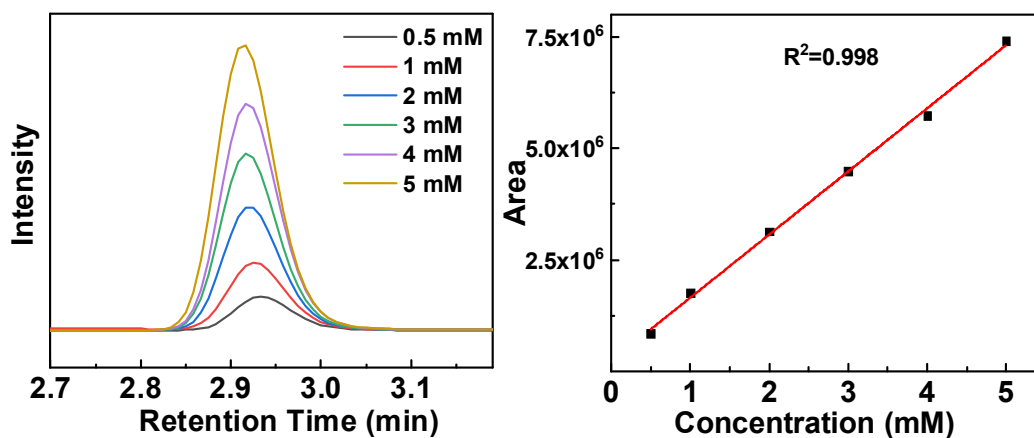


Figure S4. HPLC and standard curve of MPSO.

The blank and controlled experiment of MPS oxidation

The reaction temperature is 40 °C and the ratio is [MPS]:[H₂O₂]:[catalyst]=1:1.2:1/400. Within 180 min of the reaction time, the peak of MPS remained unchanged, and the peaks of MPSO and MPSO₂ did not appear at 2.7 min and 3.3 min, indicating the catalytic oxidation process of MPS was very slow when no catalyst was added, or HCCP-BPS was used as the catalyst. Naphthalene was added as internal standard to eliminate errors, and its retention time was 10.2 min.

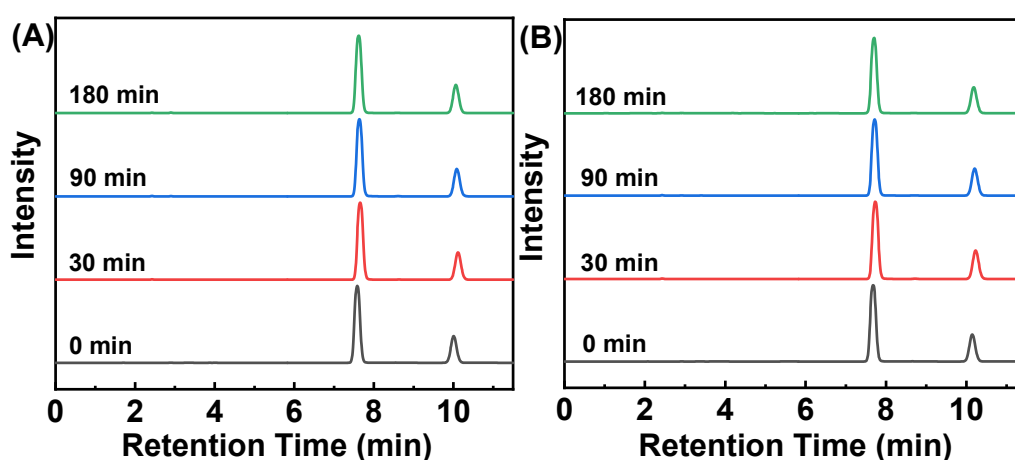


Figure S5. Catalytic oxidation of MPS with H₂O₂ as oxidant: (A) no catalyst; (B) HCCP-BPS.

¹H NMR spectra of MPS oxidation product

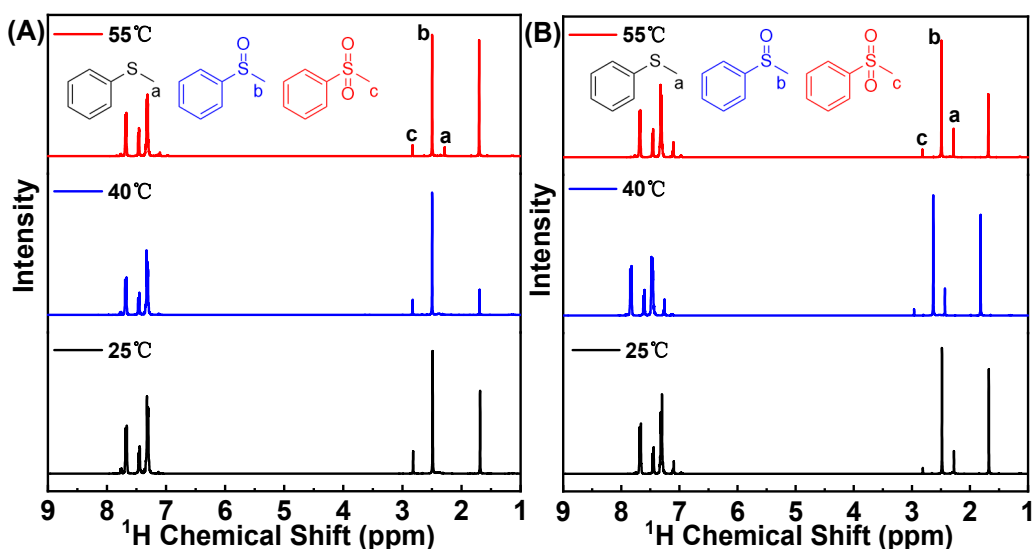


Figure S6. ¹H NMR spectra in CDCl₃ for the product of the catalytic oxidation of

MPS with different ratio of **HCCP-V** at different temperature (25 °C, 40 °C, and 55 °C): (A) 1.2 eq, (B) 1 eq.

According to the ^1H NMR spectra, it can be seen that when the oxidant equivalent is 1.2 and the reaction temperature is 25 °C, only the peaks of MPSO and MPSO₂ appear at 2.49 ppm and 2.83 ppm, indicating that anisole sulfide completely oxidized. At 40 °C, the peaks of MPSO and MPSO₂ appear at 2.49 ppm and 2.83 ppm, and the peak of MPSO₂ is weakened, indicating the selectivity improved. At 55 °C, the peaks of MPS, MPSO and MPSO₂ appear at 2.29 ppm, 2.49 ppm and 2.83 ppm, indicating MPS is not fully oxidized. At 25 °C, 40 °C and 55 °C with oxidant dosage of 1 eq, the signals of MPS, MPSO and MPSO₂ appear at 2.29 ppm, 2.49 ppm and 2.83 ppm, indicating that the oxidant dosage added is not enough. Therefore, it is proved that the optimal reaction conditions for the catalytic oxidation of MPS are oxidant 1.2 eq at 40 °C.

The HPLC standard curve of DBTSO₂

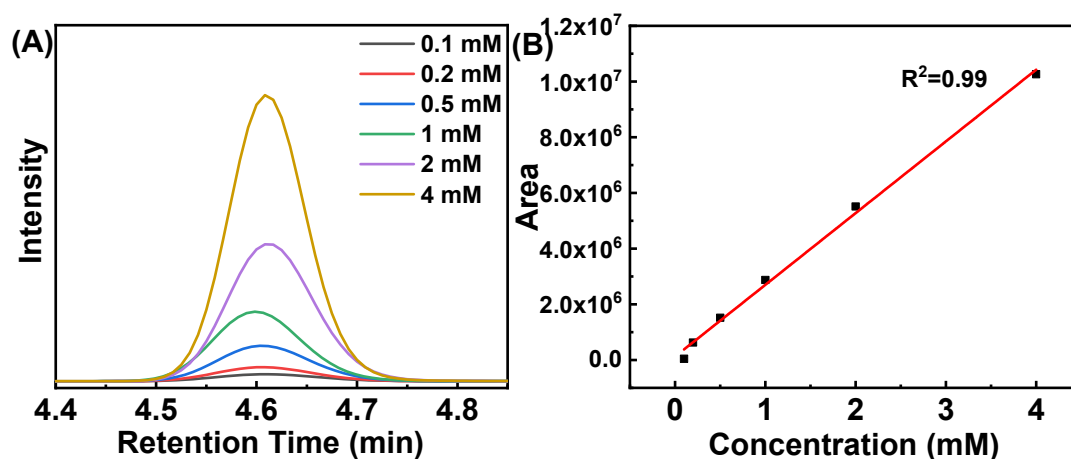


Figure S7. HPLC and standard curve of DBTSO₂.

The recycle experiment of MPS oxidation

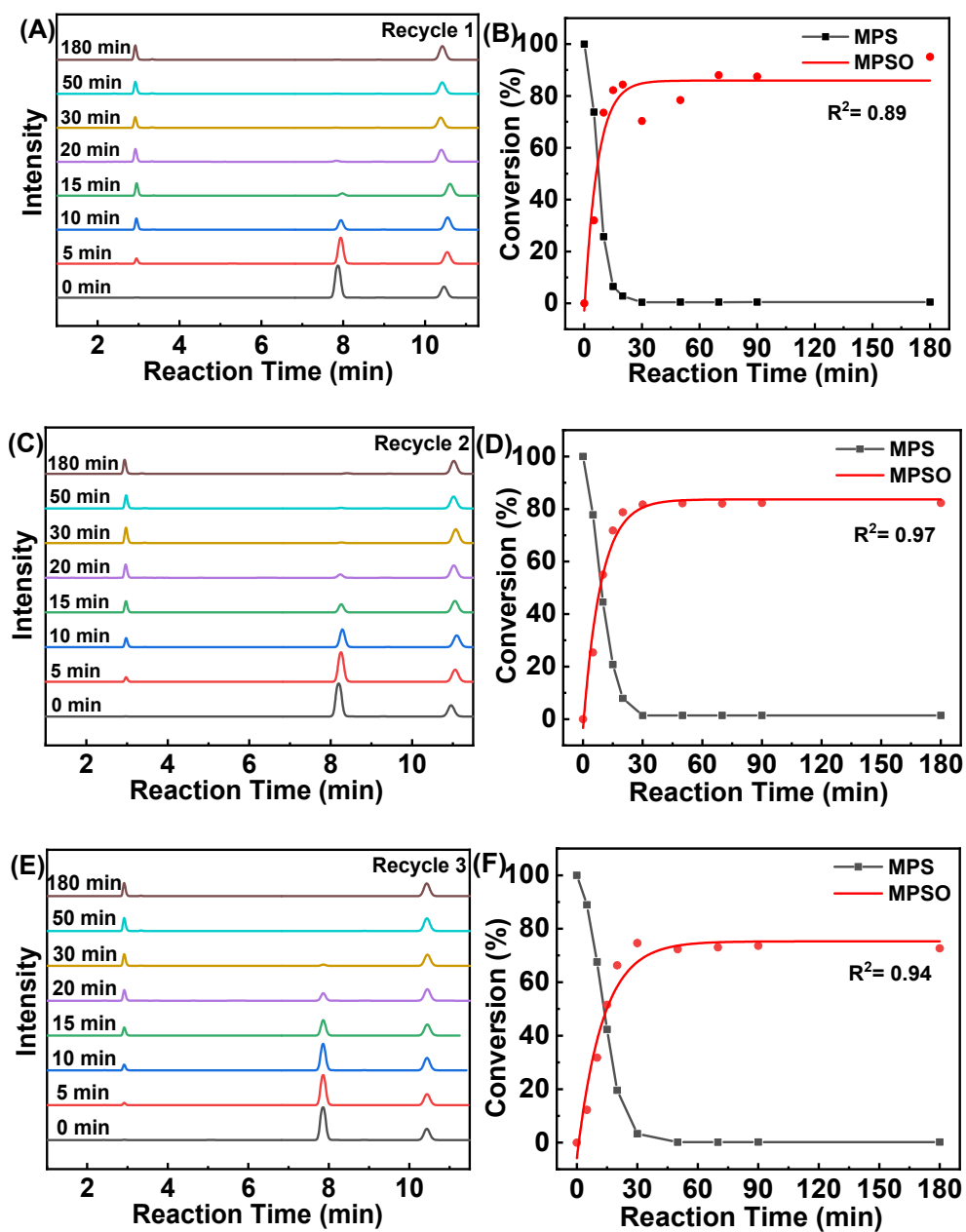


Figure S8. HPLC traces and conversion curve of MPS oxidation during recycle experiment.

Comparison with other catalysts

Table S1. Comparison with other POM-based catalysts for catalytic oxidation of different sulfides.

Catalyst	Substrate	Solvent	Temperature (°C)	[H ₂ O ₂]:[Catalyst]	Time (min)	Conv. (%)	Sel. (%) ^a	Ref.
TBA-polyV ₆	CEES	H ₂ O ₂ /EtOH	25 °C	1.2:1/20	40	100	100.0	[1]
V–Co-MOF	CEES	H ₂ O ₂ /EtOH	25 °C	1.2:1/10	10	100	100.0	[2]
[As ^{III} Mo ₆ O ₂₁ (PABA) ₃] ₂	CEES	H ₂ O ₂ /CH ₃ CN	25 °C	1.2:1/100	12	98.9	98.0	[3]
[AsMo ₆ O ₂₁ (Ala)(PHBA) ₂]	CEES	H ₂ O ₂ /EtOH	25 °C	1:3/200	5	98.5	>99.9	[4]
HCCP-V	CEES	H ₂ O ₂ /CH ₃ CN	25 °C	1.2:1/400	60	98.2	>99.9	This work
[Co ₂ Mo ₁₀ H ₄ O ₃₈]	MPS	TBHP/CH ₃ CN	40 °C	1:3/200	240	99	100.0	[5]
[V ₄ O ₁₂]	MPS	H ₂ O ₂ /EtOH	45 °C	1.2:7/200	240	98.6	98.7	[6]
[P ^{III} Mo ₆ O ₂₁ (PABA) ₃] ₂	MPS	H ₂ O ₂ /EtOH	25 °C	1.2:1/100	20	99.5	98.0	[7]
[Co(HDTBA)V ₂ O ₆]	MPS	TBHP/CH ₃ OH	50 °C	1.5:3/500	15	100	99.0	[8]
HCCP-V	MPS	CH ₃ CN	40 °C	1.2:1/400	50	99.6	>99.9	This work
[HPMo][HTAC] ₂ /SiO ₂	DBT	<i>n</i> -octane	70 °C	1.12:1	300	91	95.0	[9]
[Omim] ₃ PMo ₁₂ O ₄₀ /KIT-6	DBT	<i>n</i> -octane	60 °C	5:1	80	100	97.8	[10]
P[Vim]POM/GO	DBT	<i>n</i> -octane	60 °C	9:1	60	100	>98.0	[11]
V19/Al	DBT	diesel/CH ₃ CN	60 °C	4:1	30	98.6	>96.0	[12]
HCCP-V	DBT	CH ₃ CN	70 °C	8:1/100	50	92.2	98.9	This work

^aSelectivity to corresponding sulfoxide (CEESO, MPSO, and DBTSO₂).

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