Supplementary Materials: Two New Sandwich-Type Polyoxomolybdates Functionalized with Diphosphonates: Efficient and Selective Oxidation of Sulfides to Sulfones

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XPRD

In order to detect the purity of test sample, the powder XRD analysis of **1** and **2** has completed. In Figure S1, the powder XRD pattern of **1** and **2** (blue curve) are well in agreement with their simulated ones from X-ray single-crystal data (black curve), and peak intensity is discrepant due to the anisotropic effects of crystal. No apparent differences can be found in the patterns, implying that the sample used for all the characterization and test is pure.



Figure S1. (**a**) the simulated and experimental XRPD patterns of compound **1**; (**b**) the simulated and experimental XRPD patterns of compound **2**.

IR

The infrared spectra of the two compounds from 4000 to 500 cm⁻¹ have shown the similar between them. Here, P–O in organophosphorus characteristic vibration takes the form of the moderately strong peak and strong peak in 1180-1000cm⁻¹. Mo–Ot and Mo–O–Mo stretching vibration appears in 970-870 cm⁻¹ and 750-680 cm⁻¹ respectively. In addition, the strong band at 3430 cm⁻¹ corresponds to the stretching vibration of O–H and the sharp peak at 1640cm⁻¹ corresponds to the bend vibration of O–H in crystal water and coordinated water. The diagnostic infrared spectra have been shown at Figure S2.



Figure S2. IR spectrum of two compounds: (a) compound 1; (b) compound 2.

The representation of the synthesis of two POMs



Figure S3. (a) the {Na6} cluster; (b) polyhedral/ball-and-stick view of the monomer of compound **1**; (c) the 1D chain of compound **1**; (d) the 2D planar structure of compound 1; (MoO6/Mo: blue, P: yellow, Ni: green, C: brown, O: red, Na: cyan-blue.)



Figure S4. (a) polyhedral/ball-and-stick view of the monomer of compound **2**; (b) the 1D sodium chain; (c) the {Na₆} cluster (d) one 2D plane of compound **2**; (e) one 2D plane of compound **2** from the side view; (f) the cluster of two sodions; (g) the 3D structure of compound **2**. (MoO₆/Mo: blue, P: yellow, Co: amaranth, C: brown, O: red, Na: cyan-blue.)

Catalysis

Entry	Catalyst	T/°C	Time/h	Conversion/%	Sulfoxide	Sulfone
1 ^b	Co-POM this work	50	1	98	18	82
2	HEDP	50	1	46	25	75
3	NiCl ₂	50	1	52	29	71
4°	Na2MoO4	50	1	80	46	54
5	^a PMo ₁₂	50	1	96	50	50
6	PMo12 + NiCl2	50	1	97	90	10
7 ^d	Na2MoO4 + HEDP + NiCl2	50	1	88	61	39

 Table S1. The comparison experimental results.

^bReaction condition: catalyst, 15 μmol; thioanisole, 0.5mmol; acetonitrile, 5 mL; H2O₂, 1.25mmol. ^aPMo₁₂:

Na2HPM012O40 14H2O. ^{c, d}Na2MoO4, 60 µmol;

Catalvet	Tomporaturo	Time	Conversion	Selectivity		Roforoncos
Catalyst	Temperature	Time	Conversion	Sulfoxide	Sulfone	Kelelences
1	50	1h	08	5	04	Present
1	50	111	90	5	74	work
[Bmim]4M08O26	60	1h	100	-	>99	[1]
[PO4{WO(O2)2}4]@Im	nt	15min	04	07	2	[2]
PIILP	11	1311111	94	97	3	[2]
PDDA-SiV2W10	rt	3h	99	0	100	[3]
[-						
SiW10O34(H2O)2]4-@M	rt	3h	45	86	14	[4]
CM-41						
TBAPWFe	50	1h	99	1	99	[5]
Na10K22·1·85H2O	60	1h	99	14	86	[6]
PW11Ni-Cd-MOM	rt	18h	>99	38	62	[7]
titanium catalyst	80	2.5h	100	3	97	[8]
Fe(acac) ₂	100	2	96	94	6	[9]

Table S2. The results of the comparison with other catalysts.

Table S3. The conversion and selectivity of catalytic reaction after every run.

Runs	Conversion/%	Selectivity/%		
1	98	94		
2	97	90		
3	92	80		
4	70	62		



Figure S5. The infrared spectra of catalyst after the reactions.

Table S4. Solution	n ³¹ P NMR	chemical	shifts	of 1, 2	and HEDP.
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Compounds	³¹ P NMR Chemical Shifts / ppm		
1	26.428		
2	27.148		
HEDP	22.196		

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