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Supporting information

Synthesis, characterization of a Sb(V)-containing polyoxomolybdate serving as a catalyst for sulfoxidation

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CONTENTS

Section 1 The bond valence sum calculations

Table S1 The BVS calculations of all oxygen atoms in polyoxoanion.

Atom	BVS	Atom	BVS
O1	0.92	O7	1.23
O2	1.87	O8	1.07
O3	1.70	O9	1.06
O4	1.74	Sb1	5.27
O5	1.26	Mo1	6.03
O6	1.72	Mo2	5.99

Section 2 Selected bond lengths

Table S2 Selected bond length (Å) of compound **1**

Bond	Length	Bond	Length
Sb(1)–O(5)	1.985(9)	Mo(1)–O(5)	2.277(6)
Sb(1)–O(5)$^{\#1}$	1.985(9)	Mo(1)–O(6)	1.706(6)
Sb(1)–O(7)$^{\#1}$	1.992(6)	Mo(1)–O(7)	2.285(6)
Sb(1)–O(7)$^{\#2}$	1.992(6)	Mo(2)–O(2)$^{\#2}$	1.926(6)
Sb(1)–O(7)$^{\#3}$	1.992(6)	Mo(2)–O(2)	1.926(6)
Sb(1)–O(7)	1.992(6)	Mo(2)–O(3)$^{\#2}$	1.711(6)
Mo(1)–O(1)	1.938(4)	Mo(2)–O(3)	1.711(6)
Mo(1)–O(2)	1.938(6)	Mo(2)–O(7)	2.296(6)
Mo(1)–O(4)	1.702(6)	Mo(2)–O(7)$^{\#2}$	2.296(6)

$^{\#1}$-X, 1-Y, -Z; $^{\#2}$+X, 1-Y, -Z; $^{\#3}$-X, +Y, +Z;

Section 3 Additional structural figures

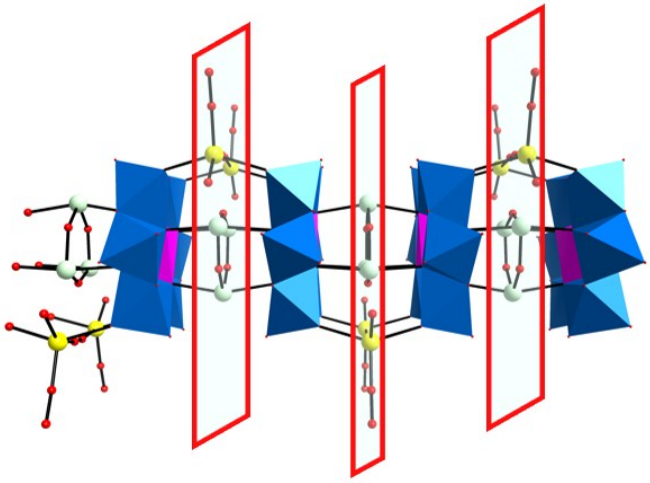

Fig. S1 The mirror-symmetry representation of adjacent Anderson-type {$SbMo_6$} units.

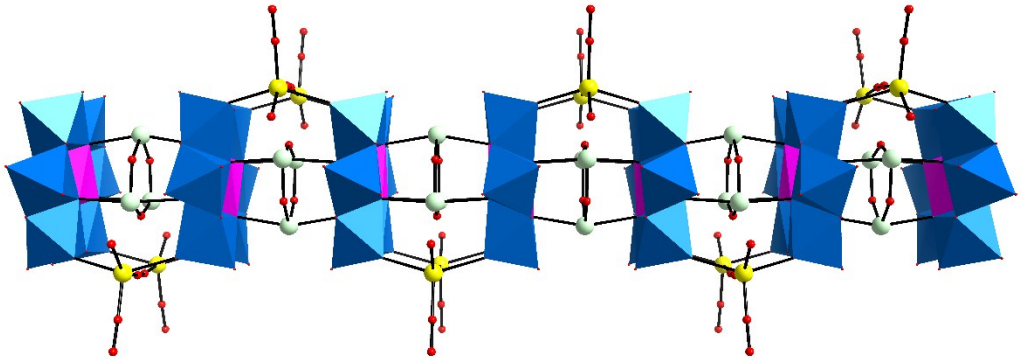

Fig. S2 The polyhedral and ball-and-stick representation of polyanion of **1** alongs the *a* direction. Color cod: Sb, cyan; SbNa, turquoise; Mo, purple, O, red, Na, yellow.

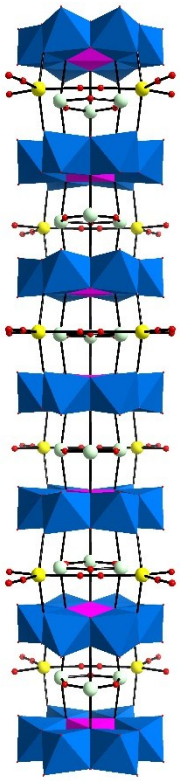

Fig. S3 The polyhedral and ball-and-stick representation of polyanion of **1** alongs the *b* direction. Color cod: Sb, cyan; SbNa, turquoise; Mo, purple, O, red, Na, yellow.

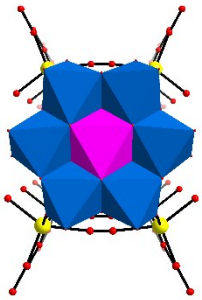

Fig. S4 The polyhedral and ball-and-stick representation of polyanion of **1** alongs the *c* direction. Color cod: Sb, cyan; SbNa, turquoise; Mo, purple, O, red, Na, yellow.

Section 4 Additional measurements

4.1 X-ray powder patterns

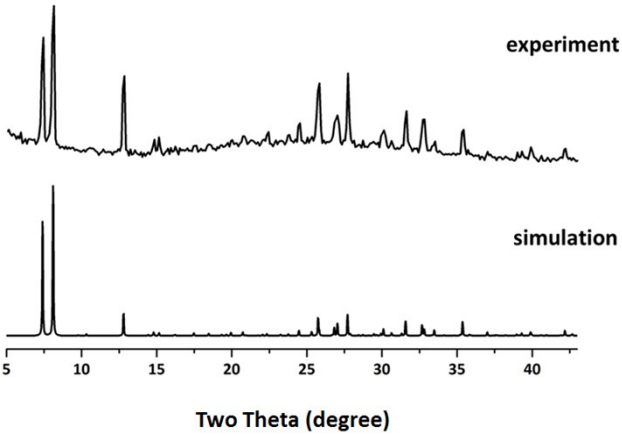

Fig. S5 The XPRD patterns for experiment (top) and simulated (bottom) of **1**.

4.2 IR Spectrum

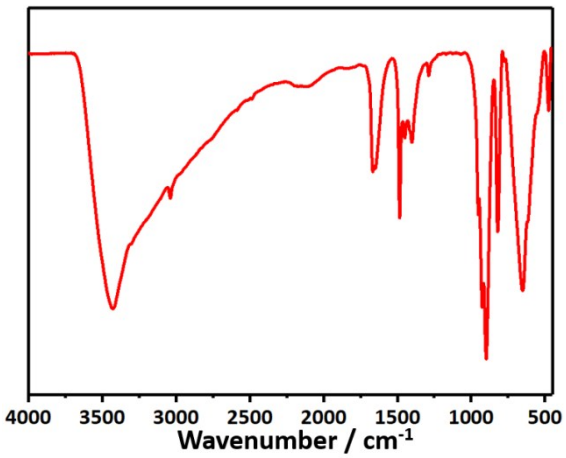

Fig. S6 The IR spectrum of compound **1**.

4.3 Thermogravimetric analysis

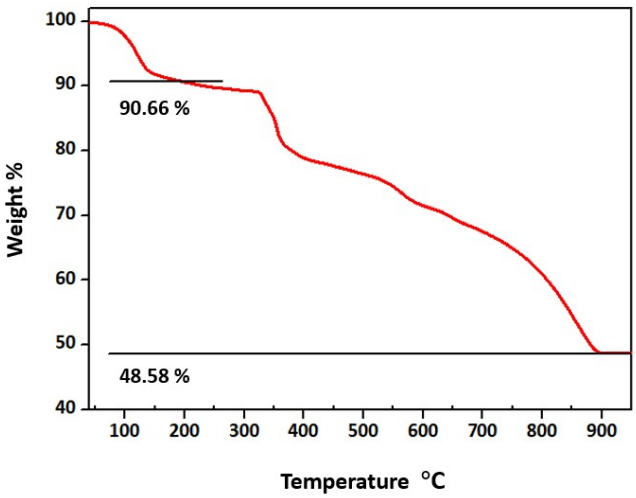

Fig. S7 Thermogravimetric curve of **1**.

Section 5 Catalytic properties

Table S3 Oxidation of sulfides with different catalysts [a]

Entry	Catalyst	H_2O_2[b]	Con.[c] (%)	Sel. (%)
1[d]	/		8.3	13.2
2	Sb_2O_3		3.9	0
3	Sb_2O_5		7.9	0
4	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$		55.6	68.9
5	$Na_2MoO_4\cdot 2H_2O$		34.4	29
6	$H_3PMo_{12}O_{40}$	3	5.8	6.4
7	$H_4SiMo_{12}O_{40}$		80.3	54.4
8	$H_6As_2Mo_{18}O_{62}$		3.4	100
9	$H_3PW_{12}O_{40}$		4.9	7.5
10	$H_4GeW_{12}O_{40}$		4.5	9.1
11	$H_4SiW_{12}O_{40}$		4.6	8.6
12	Compound **1**		100	100

[a] Reaction conditions: catalyst (0.5 mol%), substrate (1 mmol), H_2O (3 mL), 1 h, 25 °C. [b] H_2O_2/substrate ratio. [c] Determined by GC analyses based on initial substrate. [d] Blank experiment.

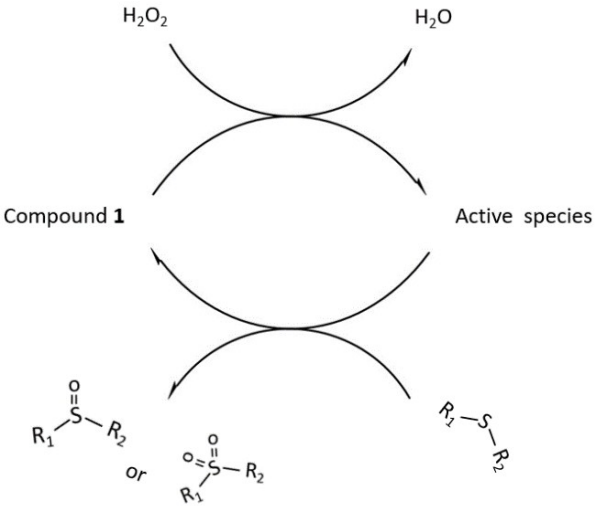

Fig. S8 Proposed mechanism for the POM-catalyzed oxidation of sulfides in water.

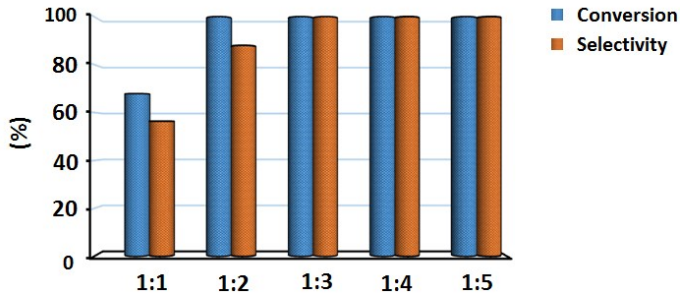

Fig. S9 Effect of different H_2O_2/ substrate molar ratios on the catalytic oxidation of thioanisole.

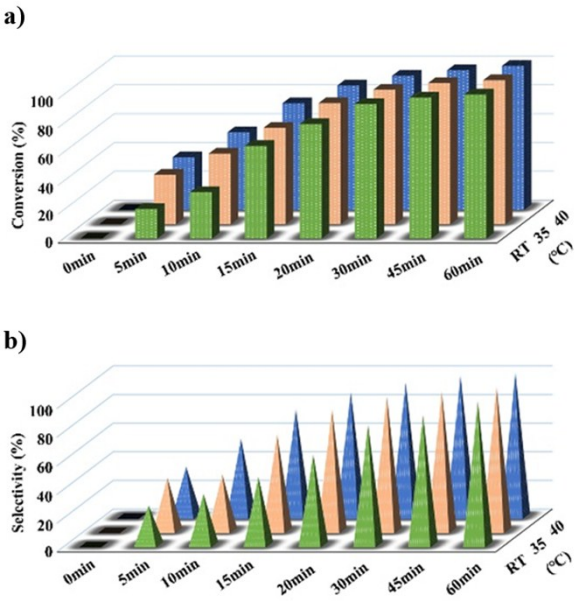

Fig. S10 (a, b) Effect of temperature on the catalytic oxidation of thioanisole.

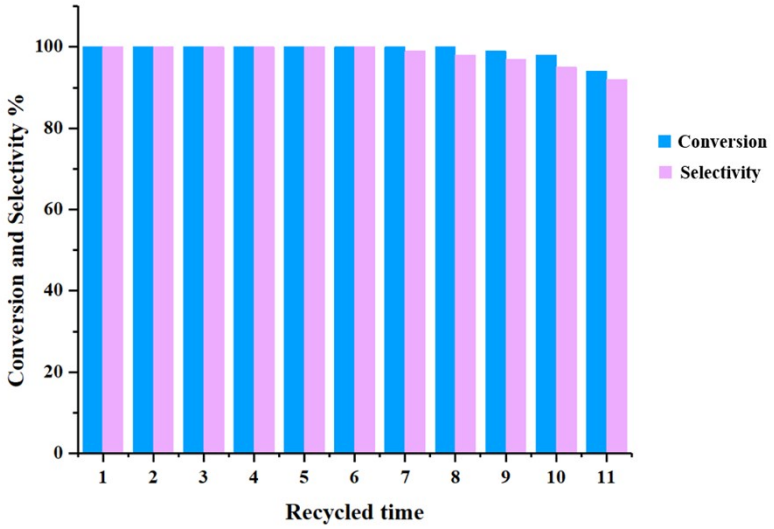

Fig. S11 Recyclability of the catalyst **1** for the oxidation of thioanisole. Reaction conditions: Catalyst (5 µmol), thioanisole (1 mmol), H_2O_2 (3 mmol), H_2O (3 mL), 25 °C, 1 h.