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Assembly of polyoxometalate-thiacalix[4]arene-based

inorganic-organic hybrids as efficient catalytic oxidation

desulfurization catalysts

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Self-assembly of polyoxometalates, Ni(II)/Ag(I)cations and tetra-[5-(mercapto)-1-methyltetrazole]-thiacalix[4]arene (L) obtained three inorganic-organic hybrids, namely, $[Ni_{3}L_{2}(CH_{3}OH)_{6}(H_{2}O)_{4}][PMo_{12}O_{40}]_{2} \cdot 3CH_{3}OH \cdot 2H_{2}O$ (1), $[Ni_{3}L_{2}(CH_{3}OH)_{6}(H_{2}O)_{4}][PW_{12}O_{40}]_{2} \cdot 3CH_{3}OH \cdot 2H_{2}O$ (2) and $[Ag_{3}L(PMo_{12}O_{40})]$ (3). In the hybrids of 1 and 2, Ni(II) cations are attached by L ligands to produce layered frameworks, and H bonds among the [PMo₁₂O₄₀]³⁻/[PW₁₂O₄₀]³⁻ anions and L ligands lengthen the structures to form 3D supramolecular architectures. Hybrid 3 exhibits a 3D architecture, of which Ag(I) cations not only coordinated with the N and O atoms of L ligands and $[PMo_{12}O_{40}]^{3-}$ anions simultaneously, but also connected each other by Ag-Ag interactions. It is worth mentioning that 1 and 3 as recycled catalysts show excellent heterogeneous catalytic activity in oxidation desulfurization reactions.

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1. Introduction

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At present, with the increase of sulfur-containing fossil fuels, environmental problems become more and more serious, and sulfur removal has received great significance.^{1,2} Hydrodesulfurization, as a traditional technique, is the main sulfur removal method in the business.^{3,4} Nonetheless, the method needs harsh conditions, such as high temperature, catalysts and high pressure.^{5,6} Also, it is not efficient enough for those heteroaromatic sulfur-compounds.⁷ So far, other methods have been developed, which involve extractive desulfurization,^{8,9} adsorption desulfurization,^{10,11} oxidation desulfurization (ODS),¹²⁻¹⁵ and biological desulfurization,¹⁶ etc. Among the above methods, ODS is an efficient and mild deep desulfurization method.^{17,18} In ODS reactions, the help of active oxidants are needed, such as hydrogen peroxide,¹⁹ molecular oxygen^{20,21} and tert-butylhydroperoxide (TBHP).²² Sulfur-containing species could be oxidized rapidly by catalysts into corresponding sulfones and sulfoxides.²³ In this regard, the synthesis of efficient catalysts is essential and highly necessary.

Polyoxometalates (POMs), defined as inorganic metal oxide clusters,^{24,25} are a kind of metal oxides with unique physical and chemical properties.²⁶⁻²⁸ It is found that POMs display promising properties in the field of oxidation catalysis,^{29,30} such as ODS.^{24,31-33} The reason is attributed to the advantages of mild reaction conditions, high efficiency, oxidation resistance and low price.³⁴⁻³⁷ But one of the most worrisome drawbacks of POMs is their excellent water-solublility, which impedes their application as recycled catalysts.³⁸⁻⁴¹ Recently, POM-based inorganic-organic hybrids were discovered application in the field of heterogeneous catalysts.⁴² Several organic ligands, such as carboxylic acid,⁴³ ionic liquids⁴⁴ and calix[4]arene^{38,45} have been used in the construction of POM-based inorganic-organic hybrid catalysts.⁴⁶⁻⁴⁸ In this regard, functional calix[4]arenes have been diffusely applied as excellent multidentate ligands, which can present great structural diversity of the hybrids.⁴⁹⁻⁵¹

Inspired by this, a characteristic thiacalix[4]arene ligand with four 5-mercapto-1-methyltetrazole groups (L, Scheme 1) was ingenious designed. By

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 $[Ni_{3}L_{2}(CH_{3}OH)_{6}(H_{2}O)_{4}][Pw_{12}O_{40}]_{2} \cdot 3CH_{3}OH \cdot 2H_{2}O$ (2) and $[Ag_{3}L(PMo_{12}O_{40})]$ (3)

were synthesized. Noticeably, 1 and 3 could be employed as efficient heterogeneous catalysts for ODS reactions.



Scheme 1 View of L ligand.

2. Experimental section

2.1. Preparation of [Ni₃L₂(CH₃OH)₆(H₂O)₄][PMo₁₂O₄₀]₂·3CH₃OH·2H₂O (1)

The mixture of H₃PMo₁₂O₄₀ (18 mg, 0.01 mmol), NiCl₂·6H₂O (10 mg, 0.04 mmol), L (12 mg, 0.01 mmol), CH₂Cl₂ (3 mL) and ethanol (1 mL) were added into a Teflon reactor (15 mL) and heated at 130 °C for 72 hours. Dark yellow crystals 1 were got (yield of 28%). Anal. Calcd for $C_{121}H_{192}N_{32}O_{103}S_{16}P_2M_{024}N_{13}$ (*Mr* = 6796.64): C, 21.38; H, 2.85; N, 6.59. Found: C, 20.85; H, 2.53; N, 6.77. IR (KBr, cm⁻¹): 3308 (w), 2966 (m), 2863 (w), 1612 (w), 1579 (w), 1547 (w), 1467 (m), 1429 (m), 1402 (w), 1380 (w), 1261 (m), 1245 (w), 1191 (m), 1067 (s), 965 (s), 873 (s), 804 (s), 703 (m), 593 (m), 507 (m) (Fig. S1⁺).

2.2. Preparation of [Ni₃L₂(CH₃OH)₆(H₂O)₄][PW₁₂O₄₀]₂·3CH₃OH·2H₂O (2)

The synthesis of 2 was similar to 1 except the H₃PW₁₂O₄₀ (29 mg, 0.01 mmol) was

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(1),

used. Pale green crystals **2** were got (yield of 27%). Anal. Caled 10. for MOP/DODT04097E $C_{121}H_{192}N_{32}O_{103}S_{16}P_2W_{24}Ni_3$ (*Mr* = 8906.48): C, 16.32; H, 2.17; N, 5.03. Found: C, 15.88; H, 1.94; N, 5.15. IR (KBr, cm⁻¹): 3369 (w), 2960 (m), 2868 (w), 1617 (w), 1584 (w), 1542 (w), 1472 (m), 1439 (m), 1407 (w), 1375 (w), 1299 (w), 1266 (m), 1234 (w), 1191 (w), 1080 (s), 979 (s), 896 (s), 819 (s), 739 (m), 706 (m), 593 (m), 521 (m).

2.3. Preparation of [Ag₃L(PMo₁₂O₄₀)] (3)

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The mixture of H₃PMo₁₂O₄₀ (18 mg, 0.01 mmol), AgNO₃ (7 mg, 0.04 mmol), L (12 mg, 0.01 mmol), acetonitrile (2 mL), ethanol (6 mL) and 4 drops of 2.3 M nitric acid were put in a Teflon reactor and heated at 130 °C for 72 hours. Dark yellow brown crystals **3** were got (yield of 18%). Anal. Calcd for C₅₆H₇₂N₁₆O₄₄S₈PMo₁₂Ag₃ (Mr = 3435.63): C, 19.58; H, 2.11; N, 6.52. Found: C, 19.60; H, 1.95; N, 6.86. IR (KBr, cm⁻¹): 3430 (w), 2960 (w), 2868 (w), 1629 (w), 1472 (w), 1440 (w), 1412 (w), 1386 (w), 1283 (w), 1267 (w), 1240 (w), 1213 (w), 1186 (w), 1061 (s), 992 (m), 954 (s), 877 (s), 807 (s), 706 (m), 599 (m), 550 (m), 502 (m), 458 (m).

The crystallographic data of 1-3 are contained in Table 1.

=			
complex	1	2	3
formula	$C_{121}H_{192}N_{32}O_{103}S_{16}P_2Mo_{24}Ni_3\\$	$C_{121}H_{192}N_{32}O_{103}S_{16}P_2W_{24}Ni_3\\$	$C_{56}H_{72}N_{16}O_{44}S_8PMo_{12}Ag_3\\$
Mr	6796.64	8906.48	3435.63
crystal system	Triclinic	Triclinic	Monoclinic
space group	<i>P</i> -1	<i>P</i> -1	C2/c
<i>a</i> (Å)	13.4965(6)	13.5204(5)	30.4234(11)
<i>b</i> (Å)	14.0075(7)	14.1184(5)	12.8113(5)
<i>c</i> (Å)	32.2487(11)	32.4331(12)	25.0925(9)
α (°)	91.811(3)	92.065(3)	90
β (°)	99.556(3)	99.761(3)	90.597(3)
γ (°)	106.631(4)	106.404(3)	90

Table 1 Crystallographic Data and Structural Refinements for 1-3

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$V(Å^3)$	5740.4(4)	5829.9(4)	9779.6(6) DOI: 10.1039/D0DT04097E
Ζ	1	1	4
D_{calc} (g cm ⁻³)	1.966	2.537	2.333
F (000)	3344	4112	6640
<i>R</i> _{int}	0.0465	0.0434	0.0391
GOF on F^2	1.030	1.016	1.124
R1 ^a [I>2σ(I)]	0.0749	0.0630	0.0879
wR_2^b (all data)	0.2224	0.1549	0.1729

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}wR_{2} = \{\Sigma [w(F_{o}{}^{2} - F_{c}{}^{2})^{2}] / \Sigma w(F_{o}{}^{2})^{2}] \}^{1/2}.$

2.4. Procedure of ODS reaction

TBHP (0.50 mmol), substrate (0.25 mmol), CH_2Cl_2 (5 mL), biphenyl (0.25 mmol) and catalyst (1: 1.47 µmol, **3**: 2.91 µmol) were put into a 38 mL pressure-proof pipe. The above mixture was stirred at 25 °C (for **1**) or 50 °C (for **3**). The conversion rate was determined by GC or HPLC. The product was further proved by ¹H NMR.

3. Results and discussion

For hybrids **1** and **2**, SQUEEZE instruction of PLATON was used. Their formula were affirmed by TGA, electron cloud density and elemental analysis (Fig. S2[†]).

3.1. Crystal structures of [Ni₃(L)₂(CH₃OH)₆(H₂O)₄][PMo₁₂O₄₀]₂·3CH₃OH·2H₂O (1) and [Ni₃(L)₂(CH₃OH)₆(H₂O)₄][PW₁₂O₄₀]₂·3CH₃OH·2H₂O (2)

The framework of **2** is isomorphic with that of **1** (Fig. S3[†]). Therefore, the framework of **1** will be described. The fundamental unit of **1** contains two halves of $[PMo_{12}O_{40}]^{3-}$ anions, one and a half of Ni(II) cations, one L ligand, two water molecules, three methanol molecules, a free water molecule, and one and a half of free methanol molecules. The $[PMo_{12}O_{40}]^{3-}$ anions serve as counter ions to balance the positive charge of the framework. The coordination environments of two Ni(II) cations are extraordinary different (Fig. 1a). Ni1 lies at an inversion center, and has a six-coordinated $[N_2O_4]$ octahedral geometry defined by two L ligands and four

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methanol molecules. Ni2 is six-surrounded by three L ligands, two water molecules/DODT04097E and one methanol molecule. L ligands connect Ni(II) atoms to yield a layered structure (Fig. 1b). As shown in Fig. 1c, the circumstances of two types of independent $[PMo_{12}O_{40}]^{3-}$ anions are different, one type lies in the channel and another scatters among the layers. There are C-H···O hydrogen-bond interactions between the $[PMo_{12}O_{40}]^{3-}$ anions and L ligands (C18-H18B···O45, C31-H31B···O32^{#3}, and C57-H57C···O36), which connect the whole structure to produce a 3D supramolecular structure (Table S1⁺).



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Fig. 1 (a) Coordination spheres of Ni(II) cations in 1. (b) 2D layered architecture. (c)3D supramolecular structure.

3.2. Crystal structure of [Ag₃(PMo₁₂O₄₀)(L)] (3)

The fundamental unit of **3** contains half of a $[PMo_{12}O_{40}]^{3-}$ anion, one and a half of Ag(I) cations and half of a L ligand. Ag1 is four-coordinated with one S atom, two N atoms from two disparate L ligands and one terminal-O atom of $[PMo_{12}O_{40}]^{3-}$ anion. Ag2 is coordinated with one N atom from L ligand and one bridge-O atom from $[PMo_{12}O_{40}]^{3-}$ anion.⁵² It is worth mentioning that Ag2 and its symmetry-related Ag2^{#1} atom form a metallic bond (Fig. 2a). The length of Ag2-Ag2^{#1} is 2.679(8) Å (Table S2†).⁵³ Ag(I) is linked by L ligands to form a planar structure (Fig. 2b). To be specific, Ag(I) ions are connected by L ligands, $[PMo_{12}O_{40}]^{3-}$ anions and its symmetry-related ions to yield a 3D architecture (Fig. 2c).



(a)

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(b)



Fig. 2 (a) Coordination environments of Ag(I) cations in **3**. (b) 2D layered architecture. (c) 3D architecture.

3.3. Catalytic performance of 1 and 3 for ODS reaction

To study the optimal condition, a series of explorations were carried out by using TBHP as oxidant, biphenyl as internal standard and methyl phenyl sulfide (MBT) as typical substrate separately (Table 2). The conversion rate of MBT was calculated by

View Article Online GC (Fig. S4 and S5⁺). Based on reported literature, Keggin-type POMs^Dpbssess/DODT04097E excellent activities to ODS reactions.⁵⁴ So firstly, the reactions were conducted by using pure H₃PMo₁₂O₄₀ and H₃PW₁₂O₄₀ as catalysts (2.94 µmol), and the conversion of 97% and 73% was obtained, respectively (entries 1 and 2). Hence, the reaction for defining optimal conditions were conducted by using hybrid 1 as catalyst. With the reaction time from 1 to 3 h at 25 °C, the conversion rates of MBT were 80%, 90% and 99%, respectively (entries 3-5). When NiCl₂·6H₂O and L ligand were used as catalysts, the conversions were 36% and 38% separately (entries 6 and 7). When no catalyst was added to the reaction, only 32% of MBT was converted to products (entry 8). Subsequently, to explore the effect of other solvents, CH₂Cl₂ was displaced by methanol and ethanol, and the conversions were 74% and 66% separately (entries 9 and 10). In order to further explore the influence of other oxidants on the catalytic ODS reaction, 30% hydrogen peroxide was added and only 26% conversion was achieved (entry 11). Hence, the optimal condition for catalyst 1 is TBHP as oxidant and CH₂Cl₂ as solvent under the reaction time of 3 h at 25 °C.

Table 2 Catalytic ODS results under various conditions

		► <u>TBHP, C</u> CH ₂ C	$\underbrace{\text{Catalyst}}_{l_2, T}$		+	o, o S
Entry	Catalyst	Oxidant	Solvent	Temp. (°C)	Time (h)	Conversion (%)
1	$H_3PMo_{12}O_{40}$	TBHP	CH_2Cl_2	25	3	97
2	$H_3PW_{12}O_{40}$	TBHP	CH_2Cl_2	25	3	73
3	1	TBHP	CH_2Cl_2	25	1	80
4	1	TBHP	CH_2Cl_2	25	2	90
5	1	TBHP	CH_2Cl_2	25	3	99
6	NiCl ₂ ·6H ₂ O	TBHP	CH_2Cl_2	25	3	36
7	L	TBHP	CH_2Cl_2	25	3	38

0

8	None	TBHP	CH ₂ Cl ₂	25	3	View Article Online 3201: 10.1039/D0DT04097E
9	1	TBHP	methanol	25	3	74
10	1	TBHP	ethanol	25	3	66
11	1	H_2O_2	CH_2Cl_2	25	3	26

Simultaneously, we also studied the catalytic ODS reaction of hybrid **3** since it also contains $[PMo_{12}O_{40}]^{3-}$ anions (Table 3, Fig. S6 and S7†). Firstly, catalyst **3** was explored under the optimal condition of **1** by using MBT as the substrate, and the conversion was only 56% (entry 1). Therefore, the optimal condition of catalyst **3** was re-explored. At 40 °C, the conversions were 69% and 85% after 2 and 3 hours, respectively (entries 2 and 3). Consequently, the temperature was raised to 50 °C, the conversions of 92% and >99% at 1 and 2 h were achieved, respectively (entries 4 and 5). To confirm the effect of catalyst **3**, blank experiment of pure TBHP was carried out, and achieved a low conversion of 41% (entry 6). Subsequently, the reactions were done in methanol and ethanol, respectively. The conversions of 62% and 74% were obtained (entries 7 and 8). Hence, the optimal reaction time of catalyst **3** is 2 h under the temperature of 50 °C.

Entry Cataly	Catalyst	Oxidant	Solvent	Temn (°C)	Time (h)	Conversion
Lifting	Cuturyst	Oniculit	Solvent Temp. (C)		Time (ii)	(%)
1	3	TBHP	CH_2Cl_2	25	3	56
2	3	TBHP	CH_2Cl_2	40	2	69
3	3	TBHP	CH_2Cl_2	40	3	85
4	3	TBHP	CH_2Cl_2	50	1	92
5	3	TBHP	CH_2Cl_2	50	2	>99
6	None	TBHP	CH_2Cl_2	50	2	41
7	3	TBHP	methanol	50	2	62
8	3	TBHP	ethanol	50	2	74

Table 3 Catalytic oxidative desulfurization results under various conditions

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To address the universality of catalysts 1 and 3, some other sulfur-containing compounds were used as the substrates (Table 4, Figs. S8 and S9⁺). The characterization of the catalyzed ODS products were performed by ¹H NMR (Figs. S10b and S10c[†]). Under the respective optimal conditions of 1 and 3, the reactions were carried out with biphenyl as the internal standard and analyzed by HPLC. When ethylthiobenzene, 4-chlorothioanisole, 4-bromothioanisole, 4-methoxythioanisole and allylphenylsulfide were used as substrates, all of the conversion rates of 1 and 3 could achieve high values of >99%, 99% or 98% (entries 1-6). The conversion rates of 4-nitrothioanisole with electron withdrawing group were only 81% for 1 and 68% for 3, which is lower than other monophenyl thioethers in the consistent condition. When the reaction time was extended to 4 h for 1 and 7 h for 3, the conversions could reach 98% and 91%, respectively (entry 7). As to the diphenylsulfide substrate, the conversion rates were 82% and 99% after 3 and 4 h for 1. For 3, after elongating the reaction time from 2 to 3 h, the conversion of 84% increased to 91% (entry 8). As showed in entries 9 and 10, the conversion rates of dibenzothiophene (DBT) and benzothiophene (BT) were 73% and 19% for 1 and 98% and 55% for 3, respectively, even after 12-h-long reactions. The results of entries 8-10 show that steric hindrance has a major impact on the conversions.⁵⁵ Both of DBT and BT have large steric hindrance, but the S electron density of DBT is higher than BT. Hence, the conversion of DBT is higher than BT for both 1 and 3, which indicates that electron density also has a significant impact on the ODS reactions.⁵⁶

Entry	Substrates	Time (h) ^a	Conversion (%) ^{<i>a</i>}	Time $(h)^b$	Conversion $(\%)^b$		
1	S S	3	99	2	>99		
2	€ S S S S S S S S S S S S S S S S S S S	3	>99	2	>99		

Table 4 The	e ODS results	of thioethers	catalyzed b	by 1^a and 3^b
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The catalytic kinetic experiments and filtration experiments were studied for 1 and 3, respectively. For 1, the conversion rate of 4-bromothioanisole elevated speedily to 79% at 1 h, and then a slow growth was observed in the next two hours (Fig. 3a). When 1 was separated after 1 h, no noticeable catalytic conversion was observed (Fig. S11[†]). For **3**, 74% of MBT was converted to the corresponding products after 0.5 h, then the conversion increased slowly to >99% in the following 1.5 h (Fig. 3b). After 3 was hot-filtered and stirred for another 1.5 h, the conversion rate of MBT was barely increased (Fig. S12⁺). ICP analysis indicates that there is no Ni(II) or Ag(I) ions leakage in the filtrates of 1 and 3, respectively. All of these proved that the ODS reaction was heterogeneous.

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Fig. 3 (a) Catalytic kinetic experiment (orange) and filtration experiment (green) of **1** by using 4-bromothioanisole as substrate. (b) Catalytic kinetic experiment (purple) and filtration experiment (pink) of **3** by using MBT as substrate.

The stability and circularity of **1** and **3** were further verified under their optimal conditions. At the end of each cycle, **1** and **3** were collected by centrifugation, washed with CH_2Cl_2 , dried and then used for the next cycle. As shown in Fig. 4a and 4b, it was found that after the isolated catalysts were reused for four times, the catalytic performances of **1** and **3** could still reach high values of 99% and 98%, respectively (Fig. S13 and S14[†]). The PXRD pattern of the newly collected **1** was consistent with the simulation data. But the curve changed a bit when **1** was placed in air for a period of time. After each recycles, the PXRD curve of reused **1** corresponded to that of placed for a period of time (Fig. 4c). This fact reveals that although the framework of **1** has a minor change, it still remains high conversion for the ODS reaction. All of the



PXRD curves of **3** completely consistent with the simulation data after each grounds/D0DT04097E (Fig. 4d).

Fig. 4 Recycling experiments of **1** (a) and **3** (b). Experimental and catalysis PXRD patterns of **1** (c) and **3** (d).

4. Conclusions

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In conclusion, three polyoxometalate-thiacalix[4]arene-based inorganic-organic hybrids **1-3** were synthesized by using a functional thiacalix[4]arene ligand with metal ions and POM anions. In the isostructures of **1** and **2**, the layered structures formed by Ni(II) cations and L ligands are linked by $[PMo_{12}O_{40}]^{3-}/[PW_{12}O_{40}]^{3-}$ anions via hydrogen bonds to generate 3D supramolecular architectures. In **3**, Ag(I) cations are coordinated with L ligands, $[PMo_{12}O_{40}]^{3-}$ anions and its symmetry-related atoms to form a 3D framework. Notably, **1** and **3** can be used in ODS catalytic reaction. The ODS catalytic experiments verified that both hybrids have excellent heterogeneous catalytic abilities.

Author Contributions

Jie Li: Investigation, software, and writing original draft. Peng Du: Visualization.Ying-Ying Liu: Data curation, validation, and writing-review & editing. Jian-FangMa: Conceptualization, funding acquisition, and resources.

Conflicts of interest

There are no conflicts to declare.

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For ESI and crystallographic data in CIF or other electronic format see DOI: ?

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Three POM-thiacalix[4]arene-based organic-inorganic hybrids have been achieved by applying a tetrazole-functionalized thiacalix[4]arene ligand. Hybrids **1** and **3** exhibit efficient catalytic abilities for oxidation desulfurization reactions.