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Article

A μ-AsO₄-Bridging Hexadecanuclear Ni-Substituted Polyoxotungstate

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ABSTRACT: A novel tetrahedral μ -AsO₄-bridging hexadecanuclear Ni-substituted silicotungstate (ST) Na₂₁H₁₀[(AsO₄)-{Ni₈(OH)₆(H₂O)₂(CO₃)₂(A- α -SiW₉O₃₄)₂}]·60H₂O (1) was made by the reactions of trivacant [A- α -SiW₉O₃₄]¹⁰⁻ ({SiW₉}) units with Ni²⁺ cations and Na₃AsO₄·12H₂O and characterized by IR spectrometry, elemental analysis, thermogravimetric analysis (TGA), and powder X-ray diffraction (PXRD). 1 contains a novel polyoxoanion [(AsO₄){Ni₈(OH)₆(H₂O)₂(CO₃)₂(A- α -SiW₉O₃₄)₂]³¹⁻ built by four trivacant Keggin [A- α -SiW₉O₃₄]¹⁰⁻ fragments linked through an unprecedented [(AsO₄)-{Ni₈(OH)₆(H₂O)₂(CO₃)₂]⁹⁺ cluster, where the tetrahedral AsO₄ acts as an exclusively μ_2 -bridging unit to link multiple Ni centers; such a connection mode appears for the first time in



polyoxometalate chemistry. Furthermore, the electrochemical and catalytic oxidation properties of compound 1 have been investigated.

INTRODUCTION

Polyoxometalates (POMs), a unique and attractive class of nanoscale metal-oxo clusters, are constituted by the condensation of the edge-, corner-, and face-sharing MO_6 polyhedral building units of early transition metals (e.g., W, Mo, V, and Nb).^{1–7} The characteristic negative charges endow them the merits of acting as multidentate O-donor inorganic ligands. Especially for lacunary POM fragments, the high reactivity of the exposed surface oxygen atoms facilitates the integration with versatile metal cations, thereby generating the functionalized metal-substituted POMs with huge potential applications.^{8–11}

Transition metal (TM)-substituted polyoxotungstates (POTs) as an important subclass have been a rather hot subject and have attracted extensive attention. Extraordinary efforts have brought the flourishing development of TM-substituted POTs that not only depend on their flexible and diversified configurations realized by the elaborate regulation of synthesis strategies but also driven by their prominent performance in the fields of magnetism, medicine, catalysis, and materials.^{12–20} The number of novel architectures constructed by various TM cations incorporated into lacunary POTs reported in the literature is constantly increasing with time. Among them, Ni-substituted POTs have been intensively explored, and representative cases of structurally, catalytically, and electrochemically intriguing Ni-substituted POTs include $[H_2{Ni_5(H_2O)_5(OH)_3(\chi-SiW_9O_{34})(\beta-SiW_8O_{31})_2]^{24-}$, $[Ni_7(H_2O)_4(OH)_6(SiW_8O_{31})_2]^{12-,21}$ $[Ni_7(OH)_4(H_2O)-(CO_3)_2(HCO_3)(A-\alpha-SiW_9O_{34})(\beta-SiW_{10}O_{37})]^{10-}$,

 $[\{\mathrm{Ni}_{6}(\mathrm{H}_{2}\mathrm{O})_{4}(\mu_{2}-\mathrm{H}_{2}\mathrm{O})_{4}(\mu_{3}-\mathrm{OH})_{2}\}(\chi-\mathrm{SiW}_{9}\mathrm{O}_{34})_{2}]^{10-,22}$ $[Ni_{9}(OH)_{3}(H_{2}O)_{6}(HPO_{4})_{2}(PW_{9}O_{34})_{3}]^{16}, 23$ $[Ni_{9}(OH)_{6}(H_{2}O)_{6}(CO_{3})_{3}(A-\alpha-SiW_{9}O_{34})_{2}]^{14-,24}$ $[{\rm Ni}_4({\rm OH})_3(A-\alpha-{\rm SiW}_9{\rm O}_{34})]_4({\rm OOC}({\rm CH}_2)_3{\rm COO})_6]^{32-,25}$ $[Ni_{12}(OH)_{9}WO_{4}(W_{7}O_{26}(OH))(PW_{9}O_{34})_{3}]^{25-,26}$ $[Ni_{14}(AleH)_{5}(Ale)_{2}(H_{2}O)_{11}(OH)_{7}(A-\alpha-SiW_{9}O_{34})]^{12},^{27}$ $[Ni_{14}(OH)_6(H_2O)_{10}(HPO_4)_4(P_2W_{15}O_{56})_4]^{34-,28}$ $\left[\left\{ N i_{4} (OH)_{3} (PO_{4}) \right\}_{4} (PW_{9}O_{34})_{4} \right]^{28-}, ^{29} \right]$ $[Ni_{12}(OH)_{9}(CO_{3})_{3}(PO_{4})(SiW_{9}O_{34})_{3}]^{24-}$ [Ni_{13}(H_{2}O)_{3}(OH)_{9}(PO_{4})_{4}(SiW_{9}O_{34})_{3}]^{25-}, and and $[Ni_{25}(H_2O)_2OH)_{18}(CO_3)_2(PO_4)_6(SiW_9O_{34})_6]^{50-.30}$ Our group has also been active in making POTs with novel architectures and excellent performance for decades using the hydrothermal technique and has obtained numerous inorganic-organic hybrid Ni-substituted POTs, representing the breakthroughs from isolation to expansion and from oligomers to polymers, such as $[Ni_6(\mu_3 - OH)_3(H_2O)_6(enMe)_3(B-a-SiW_9O_{34})]^{-,31}$ $[Ni_6(\mu_3 - OH)_3(H_2O)_3(dien)_3H_3(\alpha - P_2W_{15} - O_{56})]^{,32}$ $[{Ni_7}(\mu_3 - V_2W_{15} - V_{56})]^{-,31}$ $\begin{array}{c} O H \end{array}_{3} O_{2} (dap)_{3} (H_{2} O)_{6} \end{array} \\ \left[H_{6} Ni_{20} P_{4} W_{34} (OH)_{4} O_{136} (en Me)_{8} (H_{2} O)_{6} \right]^{6-,34} \\ \left[H_{0} Ni_{20} P_{4} W_{34} (OH)_{4} O_{136} (en Me)_{8} (H_{2} O)_{6} \right]^{6-,34} \\ \left[Ni_{6} (Tris)_{-1} + 2 N_{10} N_{10} (en Me)_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} + 2 N_{10} N_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} (H_{10} O)_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} (H_{10} O)_{10} (H_{10} O)_{10} (H_{10} O)_{10} \right]^{1-1} \\ \left[Ni_{10} N_{10} (H_{10} O)_{10} (H_{10} O)_{10} (H_{10} O)_{10} (H_{1$

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(en)₃ (BTC)_{1.5} ($B - \alpha - PW_9O_{34}$)]₈}^{12-,35} [H₂Ni₂₄P₄W₃₆(OH)₁₂O₁₃₆(enMe)₁₂(OAc)₄(H₂O)₁₂]²⁻, and [Ni(en)(H₂O)₂]₂[H₄Ni₄₀P₈W₇₂(OH)₁₈O₂₇₂(en)₁₈-(OAc)₂(WO₄)₂(H₂O)₁₈]^{8-.36} Since the properties of compounds are intricately linked to their structural features, the design and preparation of novel Ni-substituted POTs with anticipative architectures is still attractive in POM chemistry.

Additionally, it is unambiguous that there are extremely few reports where pure inorganic tetrahedral groups, such as AsO₄ and PO₄, act as bridges or connectors in the construction of ST-based aggregates, although a large number of Ni-containing STs have already been obtained to date. These findings provide us with an excellent opportunity and motivate our efforts in this field. Herein, we use $[A-\alpha-SiW_0O_{34}]^{10-}$ ({SiW_0}), Na₃AsO₄·12H₂O, and Ni salts with the participation of Na2CO3 to explore the possibility of making novel highnuclear Ni-substituted poly(STs) bridged by the tetrahedral group. The introduction of sodium arsenate affords a fundamental source to obtain the tetrahedral connector during the course of the structural construction. Adding a large amount of CO_3^{2-} not only provides a reaction system with a high pH value that is conducive to the formation of POTs with a high-nuclear Ni-oxo cluster substitution but can also cooperate with the tetrahedral AsO4 group to produce novel configurations. Fortunately, we successfully prepared a novel μ -AsO₄-bridging hexadecanuclear Ni-substituted ST $Na_{21}H_{10}[(AsO_4){Ni_8(OH)_6(H_2O)_2(CO_3)_2(A-\alpha SiW_9O_{34}_2_2$ $[\cdot 60H_2O(1)$ in which the polyoxoanion can be considered to be fabricated by an unseen [(AsO₄)- $\{Ni_8(OH)_6(H_2O)_2(CO_3)_2\}_2]^{9+}$ cluster and four $\{SiW_9\}$ fragments through 24 μ -O linkers and 12 μ_4 -O linkers. Intriguingly, the $[(AsO_4){Ni_8(OH)_6(H_2O)_2(CO_3)_2}_2]^{9+}$ cluster is composed of two equivalent $[Ni_8(OH)_6(H_2O)_2(CO_3)_2]^{6+}$ fragments that are connected by a tetrahedral μ -AsO₄ group. Furthermore, the electrochemical and catalytic oxidation properties of 1 have been investigated.

EXPERIMENTAL SECTION

Synthesis of 1. 1 was synthesized by the reactions of $Na_{10}[A-\alpha$ -SiW₉O₃₄]·18H₂O (2.995 g, 1.078 mmol), NiCl₂·6H₂O (0.702 g, 2.954 mmol), Na_2CO_3 (1.002 g, 9.453 mmol), and $[H_2N(CH_3)_2]$ ·Cl (0.704 g, 8.634 mmol) with Na_3AsO_4 ·12H₂O (0.402 g, 0.948 mmol). The mixture was dissolved in 40 mL of distilled water, vigorously stirred for 15 min (pH 9.5), sealed in a 200 mL Teflon reactor at 100 °C for 2 h, and then cooled to ambient temperature. The pH value after the reaction was 9.3. Filtering and evaporating the solution for several days resulted in green block crystals of 1. Yield: ca. 21.35% (based on NiCl₂·6H₂O). Elemental analysis calcd for 1 (%): C, 0.40; H, 1.25; N, 0.00. Found: C, 0.48; H, 1.23; N, 0.26.

RESULTS AND DISCUSSION

Synthetic Discussion. Up to now, there have been few studies on the μ -AsO₄-bridging POTs,³⁷ let alone μ -AsO₄-bridging high-nuclear Ni-containing POTs, which is mainly because the tetrahedral group usually acts as a μ_{3^-} or μ_{4^-} bridging unit to stabilize the cores of the Ni-oxo clusters rather than as a μ_2 -bridging unit to connect the Ni-substituted POTs to form larger poly(POTs).^{28–30} To overcome this obstacle, a large amount of inorganic CO₃²⁻ was purposely introduced in the synthesis process, which was expected to play the role of a stabilizer to combine with the Ni-oxo clusters; therefore, the tetrahedral AsO₄ possesses more opportunities as a μ -bridging unit to link Ni-substituted POTs. **1** was prepared under the

condition of alkalinity. Parallel experiments reveal that the pH of the reaction solution has great influence on the isolation of the target product. The pH region between 9.2 and 9.8 favors the formation of 1, and the highest yield was obtained at pH 9.5. Additionally, since the indispensable AsO_4 tetrahedral bridging group in the polyoxoanion was derived from the introduction of Na₃AsO₄·12H₂O, the effect of the amount of Na₃AsO₄·12H₂O on the assembly of the target product was also taken into account. When the dosage varied within the range of 0.300-0.550 g, 1 could be made, affording the highest yield when 0.400 g of Na3AsO4·12H2O was added. We also attempted to obtain the subunit by completely removing Na₃AsO₄·12-H₂O, but no crystalline products were isolated in such a system. Additionally, we tried to replace AsO_4 with the tetrahedral PO₄ under the same conditions, which did not yield a similar structure.

Structure Description. Single-crystal X-ray diffraction manifests that 1 crystallizes in the monoclinic space group C2/c (Table 1) and consists of a unique μ -AsO₄-bridging

Table 1. Crystallographic Data and Structure Refinement for 1

	1
empirical formula	$C_4H_{150}AsNa_{21}Ni_{16}O_{228}Si_4W_{36}$
formula weight	12075.27
crystal system	monoclinic
space group	C2/c
a (Å)	44.3458(19)
b (Å)	14.7101(6)
c (Å)	39.7346(17)
α (°)	90
β (°)	115.1840(10)
γ (°)	90
V (Å ⁻³)	23456.3(17)
Ζ	4
$\mu \ (\mathrm{mm}^{-1})$	19.136
F(000)	21720
<i>T</i> (K)	296(2)
limiting indices	$-52 \le h \le 52$
	$-17 \le k \le 17$
	$-47 \le l \le 47$
no. of reflections collected	100809
no. of independent reflections	20350
R _{int}	0.0584
data/restrains/parameters	20350/66/1449
GOF on F^2	1.007
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0446$
	$wR_2 = 0.1159$
R indices (all data)	$R_1 = 0.0525$
	$wR_2 = 0.1202$
largest difference peak and hole (e ${\rm \AA}^{-3})$	3.682, -2.736

hexadecanuclear Ni-substituted ST polyoxoanion $[(AsO_4)-{Ni_8(OH)_6(H_2O)_2(CO_3)_2(A-\alpha-SiW_9O_{34})_2}_2]^{31-}$ (1a, Figure 1a and b), 60 lattice water molecules, and 21 Na⁺ ions. Bond valence sum (BVS) calculations³⁸ demonstrate that the oxidation states of all W, As, Si, and Ni atoms are +6, +5, +4, and +2, respectively (Table S1). Furthermore, the BVS values of O15, O16, O19, O21, O25, and O28 are 1.054, 1.059, 1.097, 1.039, 1.034, and 1.094, respectively, confirming that all the μ_3 -O atoms are OH groups; the values of the terminal O35 and O41 are 0.309 and 0.299, indicating coordinate water



Figure 1. (a) The polyoxoanion 1a, (b) the simplified structure of 1a, (c) the hexadecanuclear Ni-oxo cluster $[(AsO_4)-{Ni_8(OH)_6(H_2O)_2(CO_3)_2}]^{9+}$, and (d) the simplified structure $[(AsO_4){Ni_8(OH)_6(H_2O)_2(CO_3)_2}]^{9+}$.

molecules. The $[(AsO_4){Ni_8(OH)_6(H_2O)_2(CO_3)_2(A-\alpha \mathrm{SiW}_9\mathrm{O}_{34}\mathrm{O}_2\mathrm{O}_$ where an unprecedented μ -AsO₄-bridging hexadecanuclear Ni-oxo cluster $[(AsO_4){Ni_8(OH)_6(H_2O)_2(CO_3)_2}_2]^{9+}$ (Figure 1c and d) is encapsulated by four {SiW₉} fragments through 24 μ -O from 24 W atoms and 12 μ_{4} -O from four central SiO₄ groups. Noticeably, the hexadecanuclear Ni-oxo cluster contains two types of inorganic groups, namely tetrahedral AsO₄ and triangle CO_3^{2-} , and they play the roles of connector and stabilizer, respectively, giving rise to a novel $[(AsO_4)-\{Ni_8(OH)_6(H_2O)_2(CO_3)_2\}_2]^{9+}$ cluster. To the best of our knowledge, such a linking mode is rarely present in POM chemistry. The Ni-oxo cluster [(AsO₄)- ${Ni_8(OH)_6(H_2O)_2(CO_3)_2}_2^{9+}$ can be described as a fusion of two equivalent octanuclear Ni-oxo clusters $[Ni_8(OH)_6(H_2O)_2(CO_3)_2]^{6+}$ bridged by a μ -AsO₄ linker. Each $[Ni_8(OH)_6(H_2O)_2(CO_3)_2]^{6+}$ cluster is formed by the condensation of two edge-sharing defective-cubane {Ni₄} clusters and additionally stabilized by two μ_3 -CO₃. All Ni

ions in the $[(AsO_4){Ni_8(OH)_6(H_2O)_2(CO_3)_2}_2]^{9+}$ cluster exhibit a six-coordinate octahedral geometry with Ni–O bond lengths of 2.012(7)–2.237(7) Å. Additionally, the hexadecanuclear Ni-oxo cluster can be structurally interpreted as being formed by four defective-cubane {Ni_4} clusters with the assistance of one μ -AsO₄ and four μ_3 -CO₃.

It should be noted that Hill's group has also reported a hexadecanuclear Ni-oxo cluster-substituted tetramer $[{Ni_4(OH)_3(AsO_4)}_4(B-a-PW_9O_{34})_4]^{28-}$ (2, Figure S2a).³⁹ However, several structural differences can be easily observed between them. 1a is a silicotungstate comprised of $[A-\alpha SiW_9O_{34}$ ¹⁰⁻ units, while 2 is a tungstophosphate tetramer with $[B-a-PW_9O_{34}]^{9-}$ units (Figure S2c and d). Hexadecanuclear Ni-oxo clusters are discrepant; 1a contains four defectivecubane $\{Ni_4\}$ clusters, while there are four cubane $\{Ni_4\}$ clusters in 2 (Figure S2e and f). 1a includes two types of inorganic groups (four CO₃ groupsand one AsO₄ groups) that work together to connect and stabilize the ${Ni_{16}}$ cluster, but the four AsO_4 groups in 2 support the central $\{Ni_{16}\}$ cluster. 1a possesses four coordinate water molecules, but 2 is without coordinate water molecules. The distribution motifs of the four POT units in 1a and 2 are distinguishing, exhibiting the sloping triangular pyramid configuration and the tetrahedral configuration, respectively (Figure S2g/h).

Alternatively, **1a** can be viewed as two dimeric subunits, $[Ni_8(OH)_6(H_2O)_2(CO_3)_2(A-\alpha-SiW_9O_{34})_2]^{14-}$ {Ni₈(SiW₉)₂}, that are connected via a AsO₄ tetrahedron (Figure 2a and b) in which the AsO₄ plays the role of a purely inorganic μ_2 bridging unit to realize the structure that is scarcely observed in POM chemistry. Each $\{Ni_8(SiW_9)_2\}$ subunit is comprised of two $[Ni_4(OH)_3(H_2O)(A-\alpha-SiW_9O_{34})]^{5-}$ {Ni₄(SiW₉)} segments connected by two μ_3 -CO₃ ligands (Figure 2c). In each ${Ni_4(SiW_9)}$, the trivacant ${SiW_9}$ block incorporates a defective-cubane $\{Ni_4O_3\}$ cluster in which three corner-sharing Ni atoms (Ni1, Ni2, and Ni3) at the bottom that form a triad occupy the lacunary sites of ${SiW_9}$ and are capped by the apical Ni4 atom via three μ_3 -OH and two μ_3 -CO₃. The Ni–Ni distances in the ${Ni_4O_3}$ cluster are in the range of 2.926-3.680 Å (Figure S3). Two μ_3 -CO₃ not only guarantee the junction of the Ni triad to the apical Ni but also to the corresponding Ni centers of the neighboring ${Ni_4(SiW_9)}$ segment. The dimeric ${Ni_8(SiW_9)_2}$ subunit can be also



Figure 2. (a) The polyoxoanion 1a, (b) the dimeric $[Ni_8(OH)_6(H_2O)_2(CO_3)_2(A-\alpha-SiW_9O_{34})_2]^{14-}$ subunit; (c) the $[Ni_4(OH)_3(H_2O)(A-\alpha-SiW_9O_{34})]^{5-}$ segment, (d) the $[Ni_8(OH)_6(H_2O)_2(CO_3)_2]^{6+}$ cluster, and (e) the trivacant $[A-\alpha-SiW_9O_{34}]^{10-}$ block. Color codes are as follows: $WO_{6'}$ red; SiO₄, yellow; Ni atom, bright green; O atom, red; and C atom, black.

perceived as a special sandwich configuration in which a $[Ni_8(OH)_6(H_2O)_2(CO_3)_2]^{6+}$ cluster (Figure 2d and e) is encapsulated by two {SiW₉} blocks by means of 12 μ -O and 6 μ_4 -O atoms from two {SiW₉} moieties. This {Ni₈(SiW₉)₂} subunit is somewhat similar to the structure of $[Co_8(OH)_6(H_2O)_2(CO_3)_3(A-\alpha-SiW_9O_{34})_2]^{16-}$ (3) previously reported by Mialane et al.⁴⁰ Apart from the different elements of the functional metal atoms, the most significant discrepancy that needs to be emphasized is the bridged CO_3^{2-} anion. 3 has an additional μ -CO₃ connecting to two apical Co atoms from the $\{Co_{4}\}$ clusters to further stabilize the structure, and the remaining terminal oxygen points to the outside. However, a AsO₄ group is grafted to the $\{Ni_8(SiW_9)_2\}$ subunit in the same position of 1, which not only exerts a stabilizing effect similar to the μ_2 -CO₃ anion but additionally joins the other subunit to form a tetramer (Figure S4). In addition, the polyoxoanions are arranged in the fashion of -A-B-A- along the *a* and *c* axes and show an organized -A-A-A- array along the *b* axis (Figure S5).

Electrochemical Properties. The electrochemical performance of 1 was executed in a pH 5.0 supporting electrolyte (0.5 mol L^{-1} Na₂SO₄ + H₂SO₄) by the modified CPE. As shown in Figure 3a, the CV at a scan rate of 50 mV s⁻¹ exhibits



Figure 3. (a) Cyclic voltammograms of 1 at a scan rate of 50 mV s⁻¹. (b) Graph of CAT vs the concentrations of H_2O_2 and $NaBrO_3$ for 1.

two pairs of redox waves (I/I' and II/II') in the potential region of -1.0 to 0 V, which are assigned to the redox process of the W centers in the polyoxoanion.⁴¹⁻⁴³ The corresponding mean peak potentials are -0.379 (I/I') and -0.714 V (II/II') based on the formula $E_{1/2} = (Epa + Epc)/2$ (versus the Ag/ AgCl electrode). In addition, the peak potentials become more negative under the cathodic currents of II after elevating the scan rate from 100 to 500 mV s⁻¹; the current intensities are inversely proportional to the scan rates, which manifests such that the redox process of **1** is surface-controlled (Figure S8).⁴⁴

Furthermore, the electrocatalytic properties of 1 toward the reduction of hydrogen peroxide (H_2O_2) and bromate (BrO_3^{-}) were also recorded out under the same supporting electrolyte at a scan rate of 50 mV s^{-1} . As shown in Figure S9, compound 1 has moderate electrocatalytic activities toward the reduction of H₂O₂ and BrO₃⁻. According to the method introduced by Keita, 45,46 the catalytic efficiency is defined as CAT = $[I_{\rm p}({\rm POM, substrate}) - I_{\rm p}({\rm POM})]/I_{\rm p}({\rm POM}) \times 100\%$. Based on the current of peak II (-0.769 V), the CAT values for H_2O_2 at concentrations of 0, 5 × 10⁻⁴, 1 × 10⁻³, 3 × 10⁻³, 5 × 10^{-3} , 7 × 10^{-3} , and 9 × 10^{-3} mol L⁻¹ were calculated to 0, 41.0%, 81.6%, 109.9%, 119.9%, 138.3%, and 158.2%, respectively, whereas the CAT values for BrO3⁻ were 0, 19.3%, 23.1%, 27.5%, 33.7%, 39.9%, and 46.7% (Figure 3b). These results clearly indicate that 1 has better electrocatalytic activities in regard to H_2O_2 than BrO_3^- .

Catalytic Oxidation. The catalytic oxidation of sulfides has attracted widespread and lasting attention, as the oxidation products sulfones or sulfoxides have multiple applications in many organic reactions.^{47,48} POMs have presented good catalytic activities for the oxidation of sulfides due to their unique characteristics such as multiple active sites, redox properties, high stability, etc. $^{49-51}$ Additionally, the rational selection of oxidants is also crucial in the catalytic oxidation process; H₂O₂ is considered to be a "green oxidant" and is widely favored.^{52,53} Additionally, it is generally believed that the combination of H_2O_2 and POMs can form a peroxygen active intermediate, thereby accelerating the oxidation reaction. 54,55 Herein, we explored the performance of 1 as a heterogeneous catalyst in the acetonitrile solvent using H₂O₂ as an oxidant to catalyze the oxidation of various sulfides. The conversion rate of the sulfides and the selectivity of the catalytic products, sulfoxides and sulfones, were examined by GC (Figure S10).

In this catalytic experiment, we first selected methyl phenyl sulfide (MPS) as the substrate and conducted a blank comparison experiment. It is clear that 1 has the potential as a catalyst (Table S2, entries 1 and 2). Besides, a group of parallel dynamic experiments for the catalytic oxidation of MPS were carried out to examine the heterogeneity of the catalytic process under the conditions of 60 °C, 3 mL of CH₃CN as the solvent, and 0.5 mmol substrate. As a control, the catalyst of one reaction was removed by filtration after 20 min of reaction at the reaction temperature, and then the reaction systems were sampled at intervals of 20 min. As shown in Figure 4, the conversion of MPS hardly continued to increase over time after removing the catalyst, providing strong evidence for the heterogeneous catalytic process.

Due to the unsatisfactory catalytic effect of compound 1 under the conditions of 1 h, 60 °C, and 3 O/S (91% conversion and 55% selectivity), we tried to improve the conversion and selectivity by raising the temperature, prolonging the reaction time, and increasing the amount of oxidant; finally, the optimal reaction conditions were 2 h, 70 °C, and 5 O/S (100% conversion and 100% selectivity) (Table S2). Subsequently, we conducted a series of catalytic oxidation experiments on various thioethers under the optimal conditions to verity the universality of 1 as a sulfide oxidation catalyst. In the selection of sulfide substrates, we considered the introduced electron-withdrawing or electron-donating groups (Table 2, entries 7, 10, and 11), the positions of the aryl sulfide substituents (Table 2, entries 7–9 and 11–13), the steric hindrance effect (Table 2, entries 1–3 and 4–6), etc., all



Figure 4. Dynamic conversion profiles of MPS catalyzed by 1. Red shows the removal of the catalyst during the reaction. Reaction conditions are as follows: 0.5 mmol substrate, 3 O/S, 500 S/C, and 3 mL of CH_3CN at 60 °C.

Table 2. S	Selective	Oxidation	of	Various	Sulfides
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Entry	Substrate	Time. (h)	Temp. (°C)	Cov. (%)	Selectivi RR'SO/	Selectivity (%) RR'SO/R'RSO ₂	
1	~s~	2	70	100	0	100	
2	~~~s~~~	2	70	100	0	100	
3		2	70	100	0	100	
4		2	70	100	0	100	
5		2	70	100	18	82	
6	€∽он	2	70	99	6	94	
7	`o_∕s_	2	70	100	0	100	
8	~°s~	2	70	100	0	100	
9	~~s-	2	70	100	27	73	
10	o₂n−∕⊂_≻−s∖	2	70	100	0	100	
11	Br-	2	70	100	0	100	
12	Br S-	2	70	100	1	99	
13	Br s-	2	70	100	61	39	
14		2	70	45	48	52	
15		2	70	15	6	94	

of which may have a large impact on the conversion and selectivity. The results of the catalytic oxidation for 15 sulfides under the same conditions are summarized in Table 2. It can be clearly observed that 1 shows the good catalytic activity for most of the selected sulfides and can almost completely convert these sulfides into corresponding sulfones or sulfoxides, except for thiophene sulfides (benzothiophene and dibenzothiophene). It is worth mentioning that the aryl sulfides containing electron-withdrawing or electron-donating groups, whether at the *meta* or *para* position, have an almost 100% conversion and selectivity, while the selectivity of aryl sulfides with *ortho* substituent groups is very low (2-bromothio-anisole and 2-ethoxythioanisole), which is presumably due to the steric hindrance effect (Table 2, entries 7–9 and 11–13). As far as we know, the activity of 1 for the catalytic oxidation of sulfides is superior to that of the previously reported Zr-substituted silicotungstate tetramer.⁵⁶ We speculate it may be related to the presence of more protonated oxygen atoms in the structure of 1, which is consistent with the literature.⁵⁷

Furthermore, under optimal conditions MPS was used as the substrate to investigate the cyclicity of catalyst **1**. After each reaction, the catalyst was recovered by filtration and reused in the next round. After five cycles, the catalyst still showed desirable catalytic activity. The MPS was completely oxidized, and the selectivity for MPSO₂ was as high as 97% (Figure 5).



Figure 5. Recycling of the catalytic oxidation of MPS at 70 $^\circ C$ and 5 O/S.

Moreover, the stability of 1 in the catalytic oxidation reaction was confirmed by the good consistency of the IR spectra of the catalyst before and after the reaction (Figure S11).

CONCLUSIONS

In summary, a novel tetrahedral μ -AsO₄-bridging hexadecanuclear Ni-substituted silicotungstate Na₂₁H₁₀[(AsO₄)- $\{Ni_8(OH)_6(H_2O)_2(CO_3)_2(A-\alpha-SiW_9O_{34})_2\}_2\} \cdot 60H_2O$ (1) was made. The polyoxoanion is constituted by four $[A-\alpha SiW_9O_{34}]^{10-}$ fragments linked through an unprecedented $[(AsO_4){Ni_8(OH)_6(H_2O)_2(CO_3)_2}^{9+}$ cluster. It is worth pointing out that the tetrahedral AsO₄ acts as an exclusively μ bridging unit linking multiple Ni centers to realize the whole structure, showing that such a linking mode appears for the first time in POM chemistry. In addition, 1 has a moderate electrocatalytic performance for H₂O₂ and NaBrO₃ and shows a good catalytic activity for the catalytic oxidation of various sulfides as a heterogeneous catalyst. Additionally, recycling experiments demonstrate its good conversion and selectivity over five cycles. This work not only provides us with a feasible synthetic strategy for constructing Ni-substituted POMs with novel configurations using tetrahedral AsO₄ as μ -bridging unit but also develops the application potential of Ni-substituted POMs in the field of sulfide catalytic oxidation.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00056.

Bond valences of some atoms; relevant figures; and IR, PXRD, and TG curves (PDF)

Accession Codes

CCDC 2015606 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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