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Two new polyoxoniobosilicate-based compounds: Syntheses, structures, characterizations and their catalytic properties for epoxidation and water oxidation

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ABSTRACT

Two new polyoxoniobosilicates, $Na_{12}[Cu(en)_2(H_2O)_2]_5[H_3(SiOH)_2Si_2Nb_{16}O_{54}]_2\cdot52H_2O$ (1) and $K_4[Cu(en)_2(H_2O)_2]_2[Cu(en)_2(H_2O)]_2[Cu(en)_2][SiNb_{18}O_{54}]\cdot16H_2O$ (2) (en = ethylenediamine), have been successfully prepared with the combination method of hydrothermal and solvent evaporation methods. Both the two compounds were characterized by IR, PXRD, single crystal X-ray diffraction analysis, etc. Single crystal X-ray analysis shows that compounds 1 and 2 include a Dawson-like and a crescent-like cluster, respectively. The catalytic performances of compounds 1 and 2 were evaluated for the oxidation of styrene and the oxygen evolution reaction (OER). For the oxidation of styrene, under optimized conditions, compound 2 can achieve a 93.3% conversion in 8 h with a 71.1% selectivity toward styrene oxide, while, for the OER compound 1 exhibited the higher performance, offering a stable current density of 10 mA cm⁻² at 533 mV in basic media.

1. Introduction

Although there is only about a 200-year history for the polyoxometalate (POM) [1,2], due to its various structures [3–5] and strong versatilities [6,7], it is always a crucial objective for inorganic chemistry development. Up to now, most POM studies have focused on polyoxo-tungstates (POWs), -molybdates (POMos) and -vanadates (POVs). Compared with the POMs mentioned-above, the development of the polyoxoniobates (PONbs) is later and slower, for the {Nb₆O₁₉} precursor as the only niobium source for the synthesis of most PONbs, seriously hinder PONbs' development [8]. However, the higher negative charge and special chemical properties make PONbs own more potential applications in many fields such as virology [9–11], anticancer [12–14], nuclear waste treatment [15], catalysis [16–19], photolysis [18,20–22] and electrochemistry [23–26], and more and more scientists are devoted to the study of PONbs.

The previous PONb researches mainly concentrated on the isopolyniobates (IPONbs), but the unitary structure and element limited one from exploring the properties of the PONbs to a certain extent [22, 27–29]. With the introduction of heteroatoms and transition metal complexes (TMCs), the advancement of PONbs became rapid. The first heteropolyniobate (HPONb) K_{12} [Ti₂O₂][SiNb₁₂O₄₀]·16H₂O was synthesized by Nyman et al., in 2002 [30]. After that, a series of HPONbs which include a variety of TMCs were reported [31–35]. PONbs prepared by the introduction of lanthanide metal and their fluorescent properties are also

reported [36,37]. As for the main application of POMs, the catalysis of POWs and POMos has formed a relatively mature research system [38]. However, many PONb studies still only focused on the property of the photocatalytic hydrogen production [39–43], and there are few explorations on their other catalytic properties.

Polyoxoniobosilicates, as one of the subclasses of the PONbs, could be classified into two groups based on the cluster models: {Si₄Nb₁₆O₅₆} $({Si_4Nb_{16}})$ and ${SiNb_{18}O_{54}}$ (${SiNb_{18}}$). The polyoxoniobosilicates {Si₄Nb₁₆} was first reported by Nyman et al., in 2002 [30], and then they synthesized another {Si₄Nb₁₆} PONbs of which {Si₄Nb₁₆} polyanions are combined with TMCs [44]. Subsequently, three polyoxoni obogermanates with $\{Ge_4Nb_{16}\}$ which has the identical cluster model to ${Si_4Nb_{16}}$ as the cluster were reported by Zhang and Wang et al. [21]. and Liu et al. [45]., two of them are dipolymers constructed out of $\{Ge_4Nb_{16}\}$ and TMCs [21,45], while the other one is composed without the transition metal [45]. In comparison with the {Si₄Nb₁₆} model, the {SiNb₁₈} polyoxoniobosilicate emerges later. Around 2012, Nyman et al. reported a series of {SiNb18} PONbs with alkali metal ions as counter cations [46]. And then, organic-inorganic hybrid polyoxoniobates were consecutively synthesized with $\{SiNb_{18}\}$ as clusters and $[Cu(en)_2]^{2+}$ as TMCs [47,48]. Just like the {Si₄Nb₁₆} compounds, there were also {GaNb₁₈} and {AlNb₁₈} which have the identical cluster model to ${SiNb_{18}}$ as the cluster were reported [49].

Here, we reported two new organic-inorganic hybrid polyoxoniobosilicates based on the integrations of the two above-mentioned

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different clusters and the similar transition metal complexes. The cluster of the Na₁₂[Cu(en)₂(H₂O)₂]₅[H₃(SiOH)₂Si₂Nb₁₆O₅₄]₂·52H₂O (1) is a Dawson-type cluster. However, K₄[Cu(en)₂(H₂O)₂]₂[Cu(en)₂(H₂O)]₂[-Cu(en)₂][SiNb₁₈O₅₄]·16H₂O (2) has a crescent-like cluster which is formed by two Lindqvist {Nb₆O₁₉} units and a {SiNb₆O₂₆} fragment. For POMs are widely used as oxidation catalysts [50,51] and recently some groups also employed some POMs as OER catalysts [52–54], in this manuscript, we characterized not only the structures of the two new compounds, but also their catalytic properties for the oxidation of styrene and oxygen evolution reaction (OER).

2. Experimental

2.1. Chemical reagents and instruments

All the chemicals were of reagent grade and used without further purification. Infrared spectra were recorded as KBr pellets on a PerkinElmer Spectrum One FTIR spectrophotometer. Powder XRD patterns were obtained with a Scintag X1 powder diffractometer system using Cu K α radiation with a variable divergent slit and a solid-state detector. The electrochemical measurements were carried out on a CHI 760E electrochemical workstation. K₇HNb₆O₁₉·13H₂O was prepared as described in the literature [55].

2.2. Synthesis

 $Na_{12}[Cu(en)_2(H_2O)_2]_5[H_3(SiOH)_2Si_2Nb_{16}O_{54}]_2.52H_2O$ (1) Compound 1 was synthesized by a combination method of hydrothermal and evaporation methods. K₇HNb₆O₁₉·13H₂O (0.25g, 0.18 mmol), Cu(CH₃₋ COO)2·H2O (0.133g, 0.67 mmol), Na2SiO3·9H2O (0.033g, 0.12 mmol), Sb₂O₃ (0.013g, 0.050 mmol), en (0.33 ml) were dissolved in 8.00 ml $Na_2CO_3/NaHCO_3$ buffer solution (1 M, PH = 10). The resulting purple blue solution was adjusted to pH = 12 with a 3 M KOH solution, and it was then transferred to a Teflon-lined stainless steel autoclave (18 mL). The autoclave was heated at 140 °C for 72 h, and cooled to room temperature at a rate of 10 °C h⁻¹, then the resulting solution was filtered and evaporated at room temperature. Deep purple single crystals were obtained after 5 days. Yield (40% based on Nb). Anal. Calcd for H₂₁₄C₂₀Cu₅Na₁₂N₂₀Nb₃₂O₁₇₄Si₈: Nb, 40.66; Cu, 4.35; Si, 3.07; Na, 3.77; C, 3.29; N, 3.83; H, 2.95%; found: Nb, 40.58; Cu, 4.22; Si, 3.01; Na, 3.55; C, 3.38; N, 3.50; H, 2.66%. IR (KBr, cm⁻¹): 3019 (w), 1584 (w), 1342 (w), 1277 (w), 1048 (w), 929 (w), 881 (m), 811 (m), 719 (m), 502 (m).

 $K_4[Cu(en)_2(H_2O)_2]_2[Cu(en)_2(H_2O)]_2[Cu(en)_2][SiNb_{18}O_{54}]$ 16H₂O (2) Compound 2 was synthesized by a combination method of hydrothermal and evaporation methods, too. K₇HNb₆O₁₉·13H₂O (0.25g, 0.18 mmol), Cu(CH₃COO)₂·H₂O (0.10g, 0.50 mmol), Na₂SiO₃·9H₂O (0.013g, 0.050 mmol), Sb₂O₃ (0.020g, 0.070 mmol), en (0.33 ml) were dissolved in 8.00 ml $Na_2CO_3/NaHCO_3$ buffer solution (0.5 M, PH = 10). The resulting purple blue solution was adjusted to pH = 12 with a 3 M KOH solution, and it was then transferred to a Teflon-lined stainless steel autoclave (18 mL). The autoclave was heated at 140 °C for 72 h, and cooled to room temperature at a rate of 10 °C h⁻¹, then the resulting solution was filtered and evaporated at room temperature. Deep purple single crystals were obtained after 7 days. Yield (52% based on Nb). Anal. Calcd for C₂₀H₁₂₄Cu₅K₄N₂₀ Si Nb₁₈O₇₆: Nb, 41.44; Cu, 7.87; Si, 0.70; K, 3.88; C, 5.95; N, 6.94; H, 3.10%; found: Nb, 41.22; Cu, 7.97; Si, 0.81; K, 3.60; C, 5.66; N, 6.82; H, 3.05%. IR (KBr, cm⁻¹): 3243 (w), 1601 (m), 1460 (w), 1378 (w), 1107 (w), 1047 (m), 962 (w), 873 (s), 713 (s), 506 (s).

Preparation of the working electrode: 12 mg of graphite powder, 4 mg of catalyst and 6 μ l Nujol were mixed and ground in an agate mortar for 10 min (all of the catalysts in the corresponding ratio by weight with 25%). The blank CPE was prepared in the same procedure without the catalyst using only 16 mg graphite powder. The homogenized paste was firmly packed into a poly (tetrafluoroethylene) tube (surface area = 0.07 cm²) and the tube surface was wiped with pan paper. Electrochemical

measurements were performed with a CHI 760e electrochemical workstation and electrolyte is the 1 M KOH with saturated oxygen. Before the LSV test, 50 circles cyclic voltammetry (CV) was performed at the scan rate of 5 mV s⁻¹ to stable the working electrode and all of the LSV experiments were carried out with 1 mV s⁻¹ scan rate. All potentials reported in this work were against the reversible hydrogen electrode (RHE), which they were converted from the Ag/AgCl (3 M KCl) scale. The current densities were calculated using the geometric surface area (0.07 cm²) and the overpotential (η) was obtained using the equation of $\eta = E_{RHE} - 1.23$ V.

Catalysis. The epoxidation reactions were carried out in 5 mL twoneck borosilicate microreactors with a magnetic stirrer and a reflux condenser. The microreactors containing the olefin and solvent were immersed in the thermostated oil bath and preheated to the desired reaction temperature (60, 70, 80 °C) for 10 min prior to the addition of the oxidant solution; the addition of the oxidant was taken as the initial instant of the catalytic reaction. Initial molar ratios of catalyst/olefin/ TBHP were typically 1:3704:7408 or 1:2000:4000. CH₃CN or EtOH was added as solvent. In a typical run, the catalyst (compound 1 (2.00 mg, 0.27 µmol), compound 2 (2.00 mg, 0.50 µmol), 0.114 ml (1.00 mmol) of styrene, and 2.00 ml of solvent were added to the 5 ml two-neck flask with stirring and refluxing. The mixture was heated to a certain temperature and then TBHP was injected to start the oxidation reaction. The evolutions of the catalytic reactions were monitored using a gas chromatograph (Shimadzu, GC-8A) equipped with a FID detector and a capillary column (ZHD SE-54, 30 m \times 0.53 mm \times 1.0 $\mu m)$ and the content of relative percentage of each ingredient was determined by the gas chromatography area normalizing. In oxidation reactions of other organic substrates like cyclohexene, cyclooctene and 1-octene, all the procedures are identical with the exception of different organic substrate (with identical moles to styrene) and toluene as internal standard added in the catalytic system. Reaction products were identified by comparison with authentic samples and GC-MS (ThermoFisher Scientific Trace Dsq) with He as carrier gas.

2.3. X-ray crystallography

The crystal structures of compounds **1** and **2** were determined by single crystal X-ray diffraction. The intensity data of compounds **1** and **2** were collected on a Bruker Smart-CCD diffractometer equipped with a Mo K α radiation ($\lambda = 0.71073$ Å). No crystal showed evidence of crystal decay during data collections. The two structures were solved by direct methods and refined using full-matrix least squares on F₂ with the SHELXS-2014/7 and SHELXTL-2014/7 crystallographic software package via the Olex. 2 interface. In final refinements, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms of en were placed in calculated positions and included in the structure factor calculations but not refined, while hydrogen atoms of water molecules were not added. A summary of the crystallographic data and structure refinements for compounds 1 and 2 is shown in Table 1. CCDC number: 2036404 for compound **1**, 2036405 for compound **2**.

3. Results and discussion

3.1. Syntheses

Hydrothermal and solvent evaporation are two of the most commonly used methods for crystal synthesis and growth, and both methods have their own advantages. As for the hydrothermal synthesis, due to the particularity of the synthesis conditions (high temperature and pressure), some crystals with specific structures are usually formed [56–59]. By contrast, the room temperature evaporation synthesis is easy to generate some high-nuclear compounds because lower temperature result in a slower nucleation speed [60]. The combination of the two synthesis methods can better integrate the advantages of the two methods, thereby synthesizing more interesting crystals with diversified structures and

Table 1

Crystal data and structure refinements for compose	unds 1 and 2.
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a: $R1 = \sum ||Fo| - |Fc|| / \sum |Fo|$. b: $wR2 = \{\sum [w(Fo2?Fc2)2] / \sum [w(Fo2)2]\}1/2$.

	Compound 1	Compound 2
Empirical formula	$H_{214}C_{20}Cu_5Na_{12}N_{20}Nb_{32}O_{174}Si_8\\$	C ₂₀ H ₁₂₄ Cu ₅ K ₄ N ₂₀ SiNb ₁₈ O ₇₆
Formula weight	7311.31	4035.95
Crystal system	orthorhombic	monoclinic
Space group	Pnnm	12
a/Å	14.7897(9)	18.8861(8)
b/Å	25.2546(16)	14.7009(6)
c/Å	30.1299(16)	20.2083(8)
α (°)	90	90
β (°)	90	98.941(3)
γ (°)	90	90
Volume/Å3	11253.8(12)	5542.5(4)
Z	2	2
D _C (mg m-3)	2.158	2.418
$\mu/mm-1$	2.196	2.985
F(000)	6834.0	3930.0
Reflections	62645	11153
Reflections unique	10140	7920
R(int)	0.0360	0.0178
Parameters	698	657
GOF on F2	1.067	1.059
$R_{a} [I > 2\sigma(I)]$	$R_1 = 0.0943$	$R_1 = 0.0257$
R _b (all data)	$wR_2 = 0.2514$	$wR_2 = 0.0723$

functions. In addition to that, using buffer solution as a solvent is also a common strategy in crystal synthesis, and it generally serves as a good controller to make the system in a relatively stable pH environment [61]. In the synthesis of compounds 1 and 2, although the buffering capacity of the buffer solution was exceeded by adding too much strong alkali, the introduction of the buffer solution is still very necessary. There is nothing target crystal formed in the absence of the buffer solution, so we speculate that the buffer solution may play an obbligato role in a certain process of crystal formation. As we can see although the Sb₂O₃ was added to the reaction system, it did not participate in the formation of the crystals, perhaps it may be due to the fact that the Sb₂O₃ does not have a good solubility in this reaction solutions.

3.2. Crystal structure of compound 1

The single-crystal X-ray diffraction analysis shows that compound 1 crystallizes in the orthorhombic space group Pnnm. As for the cluster, the slow crystallization process led it to form a middle-size polyanion which is distinguished from the most common PONb types like Keggin and Lindqvist ones. According to the atomic numbers and the structure, the cluster $[H_3(SiOH)_2Si_2Nb_{16}O_{54}]^{11-}$ in compound 1 is more like a Dawson one with 18 addenda atoms and 2 center heteroatoms. There are two Si atoms replacing two adjoining Nb addenda atoms of the Dawson cluster, the substitution thus led the whole Dawson-like cluster of compound 1 to have a marked distortion (Fig. 1(a)). There are two kinds of terminal and three kinds of bridging oxygens in the Dawson-like $[H_3(SiOH)_2Si_2Nb_{16}O_{54}]^{11-}$. The terminal oxygens can be divided into two in terms



Fig. 1. (a) Ellipsoid representation of the Dawson-like cluster in compound 1; (b) ellipsoid representation of the Dawson-like cluster and sodium cluster in compound 1; (c) the 1-D chain structure formed by the cluster and the sodium ions in compound 1.

of Nb-O_t with distances of 1.75(1)-1.78(1)Å and Si-O_t with distances of 1.61(2)-1.63(2)Å, while the bridging oxygens can be grouped as: Si-O_b-Si with a Si–O distance of 1.660(7)Å, Si-O_b-Nb with Si-O_b distances of 1.591(9)-1.66(1)Å and Nb-O_b distances of 2.02(1)-2.47(1)Å, and Nb-O_b-Nb with Nb–O distances of 1.84(1)-2.17(1) Å.

The asymmetric unit is composed of half a $[H_3(SiOH)_2Si_2Nb_{16}O_{54}]^{11-2}$ two and two halves Na^+ ions, one and a quarter of $[Cu(en)_2(H_2O)_2]^{2+}$, and 13 dissociated water molecules. The two and two halves Na⁺ ions could be classified into two groups, Na(1), Na(2) and Na(3) belong to one group, while Na(4) forms the other group by itself. Na-O distances of the former group are 2.38(1)-2.95(2)Å. Na(1) is entrapped in the pit of [H₃(SiOH)₂Si₂Nb₁₆O₅₄]¹¹⁻, and interacts with four bridging oxygens from two {SiO₄} of $[H_3(SiOH)_2Si_2Nb_{16}O_{54}]^{11-}$ and two oxygens from two water molecules. The two water oxygens as bridges, at the same time, connect two Na(1) from two neighboring $[H_3(SiOH)_2Si_2Nb_{16}O_{54}]^{11-}$, forming a novel dipolymer. Except the Na(1) bridges, a pair of Na(2) as two bridges simultaneously connect two terminal oxygens from two {SiO₄} of two [H₃(SiOH)₂Si₂Nb₁₆O₅₄]¹¹⁻, indicating that the pair of Na(2) plays the same role of the water oxygens attached to Na(1). It should be noted that there are two such pairs of Na(2) sandwiched by the two $[H_2(SiOH)_2Si_2Nb_{16}O_{54}]^{11-}$. Each Na(2) is three-coordinated by two terminal oxygens from two $[H_3(SiOH)_2Si_2Nb_{16}O_{54}]^{11-}$ as well as one water molecule. In addition, Na(3) is attached to two terminal oxygens from two {NbO₅} of the two $[H_3(SiOH)_2Si_2Nb_{16}O_{54}]^{11-}$, that is to say, the Na(3) also as a bridge links the two [H₃(SiOH)₂Si₂Nb₁₆O₅₄]¹¹⁻. There are four such Na(3), each two of which are linked by a water oxygen, acting as the two-sodium-bridge connecting the two adjoining H₃(SiOH)₂Si₂Nb₁₆O₅₄]¹¹⁻. Each Na(3) is sixcoordinated by two terminal oxygens from two [H₃(SiOH)₂Si $_2Nb_{16}O_{54}]^{11-}$ as well as four water molecules. Therefore, there are two Na(1), four Na(2) and four Na(3) are sandwiched by the two $H_3(SiOH)_2Si_2Nb_{16}O_{54}]^{11-},$ forming a novel dipolymer, as depicted in Fig. 1(b). The two Na(1), four Na(2) and four Na(3) give rise to a $\{Na_{10}\}$ bridge joins two {Si₄Nb₁₆}, forming the novel dipolymer. In addition, the shortest distance between two Na(2) is 3.09(2)Å, which is comparable to the previously reported Na-Na distances [44,62].

Besides that, Na(4) is coordinated by 7 oxygens, four terminal ones originate from two adjacent dipolymers, and the other three are dissociated water molecules with Na–O distances in the range of 2.54(5)-2.84(1)Å. As shown in Fig. 1(c), two Na(4) as two inorganic bridges simultaneously connects two dipolymers to construct a novel 1-D chain structure.

Except for the sodium metals, two $[Cu(en)_2(H_2O)_2]^{2+}$ surround the cluster. The Cu belongs to $[Cu(en)_2(H_2O)_2]^{2+}$ which exhibits an octahedral geometry with four nitrogens from two en and two oxygens from two water molecules with Cu–N distances in the range of 2.00(1)-2.02(1) Å and Cu–O distances of 2.5856(1)-2.7093(1)Å. Along the a axis, the Cu-en complexes and cluster present a highly organized arrangement, each of the clusters was surrounded by eight symmetrical $[Cu(en)_2(H_2O)_2]^{2+}$.

Because the last synthesis step is evaporation, there are many dissociated water molecules in compound **1**, and thus a large number of hydrogen bonds exist. There are strong N–H···O interactions between nitrogens of copper fragments and oxygens of water molecules and PONbs with N···O distances in the range of 2.983(19)-3.274(16) Å. And there also exist many C–H···O interactions between carbons of copper fragments and oxygens of water molecules with C···O distances in the range of 3.25(3)-3.45(4) Å. However, the number of O–H···O hydrogen bonds is the largest, and the O···O distances of O–H···O interactions between water molecules and oxygens from PONbs are of 2.59(3)-3.12(6)Å, while the O···O distances of O–H···O interactions between any two close water molecules are of 2.89(3)-2.91(3)Å. Therefore, via the linking of these strong hydrogen bonds, copper fragments, water molecules and PONbs are connected to form a supramolecular structure.

Nyman et al. reported a compound [44] that is structurally very similar to compound **1**. However, detailed analysis of the two structures found that there are some differences between the two. Firstly, the numbers of the sodium and the dissociated water molecules of the two

compounds are different, leading to two different formulas. Secondly, the space group of our compound is Pnnm, but the Nyman's space group is Pnn2. The higher symmetry space group of our compound indicates that the two compounds are different. We also tried to solve the crystal structure of compound 1 using the space group Pnn2. The resulting R value (0.0891) of the space group Pnn2 is even relatively a little lower than that of Pnnm (0.0943). However, we still choose Pnnm as the right one, the reasons are listed as below: (a) we must use many hard restraints to refine the structure when using Pnn2 as the space group; (2) the Pnn2 structure showed a Flack parameter of 0.46(10); (3) many solvent molecules cannot be found in the Fourier maps when using Pnn2 as the space group; and (4) most importantly, Pnnm is a higher symmetry space group. The cif result of Pnn2 is also supplied in the supporting information for comparison.

3.3. Crystal structure of compound 2

The single-crystal X-ray diffraction analysis shows that compound **2** crystallizes in the monoclinic space group I2. There are half a $[SiNb_{18}O_{54}]^{14-}$, a $[Cu(en)_2(H_2O)_2]^{2+}$, a $[Cu(en)_2(H_2O)]^{2+}$, a $[Cu(en)_2]$ ²⁺, one and two halves of K⁺, and 8 dissociated water molecules in the asymmetric unit of compound 2. As for the cluster in compound 2, although both compounds 1 and 2 are prepared from the same sources of $\{Nb_6O_{19}\}$, compound 2 reserved two whole Lindqvist units in its cluster. And the two {Nb₆O₁₉} units with a unique hexavacant {B-SiNb₆O₂₆} Keggin fragment by corner-sharing form the complete [SiNb₁₈O₅₄]¹⁴⁻cluster which has a crescent-like shape, as depicted in Fig. 2(a). There are five types of oxygens in the $[SiNb_{18}O_{54}]^{14-}$: O_t, μ_2 -O, μ_3 -O, μ_4 -O, and μ_6 -O. Fourteen O_t each are only connected to a Nb with Nb–O distances of 1.752(5)-1.782(5)Å; thirty six μ_2 -bridging O each coordinate with two Nb atoms with Nb-O distances of 1.812(5)-2.130(6) Å; two µ₃-bridging O each connect two Nb and one Si atoms with Nb–O distances of 2.191(5)-2.197(5)Å and a Si-O distance of 1.657(5)Å; two µ4-O each join three Nb and one Si atoms with Nb-O distances of 2.362(5)-2.514(5)Å and a Si-O distance of 1.623(5)Å, and two central μ_6 -O each are linked to six Nb atoms with Nb–O distances of 2.226(5)-2.529(5) Å.

Besides that, K(1) is seven-coordinated by four oxygens from a $[SiNb_{18}O_{54}]^{14-}$ and three oxygens from three water molecules, indicating that K(1) is supported by the [SiNb18O54]14-, while K(2) is eight-coordinated by six oxygens originating from a [SiNb18O54]14- and two oxygens from two water molecule with K–O distances of 2.919(6)-3.06(2)Å, meaning that K(2) is located in the pit of the crescent-like cluster. K(3) is seven-coordinated by three oxygens from a [SiNb18O54]¹⁴⁻ and three oxygens from three water molecules, that is to say, K(3) acts as a bridge linking two neighboring [SiNb₁₈O₅₄]¹⁴⁻ to form a 2-D extended framework structures. As shown in Fig. 2(b), each [SiNb₁₈O₅₄]¹⁴⁻ is connected to four K(3), while each K(3) is linked to two [SiNb₁₈O₅₄]¹⁴⁻, thus, via the connections between K(3) and [SiNb₁₈O₅₄]¹⁴⁻, a novel 2-D framework structure was constructed.

The three crystallographically different copper ions form three different coordination complexes: $[Cu(en)_2(H_2O)_2]^{2+}$, $[Cu(en)_2(H_2O)_2]^{2+}$ and $[Cu(en)_2]^{2+}$. Cu(1) of $[Cu(en)_2(H_2O)_2]^{2+}$ exhibits an octahedral geometry with four nitrogens from two en and two oxygens from two water molecules with Cu–N distances in the range of 1.987(8)-2.012(9)Å and Cu–O distances in the range of 2.6296(1)-2.7078(1)Å. Cu(2) of $[Cu(en)_2(H_2O)]^{2+}$ shows a square-pyramidal geometry with four nitrogens from two en and one oxygens from one water molecules with Cu–N distances in the range of 1.996(9)-2.01(1) Å and a Cu–O distance of 2.4816(1) Å. And both the Cu(1) and Cu(2) complexes only served as the charge compensation and space filling agents. However, the Cu(3) of the metal complex $[Cu(en)_2]^{2+}$ which is not only linked to four nitrogens from two en but also axially linked to two oxygens from two clusters plays a key role in the whole structure with Cu–N distances in the range of 2.006(9)-2.017(9) Å and a Cu–O distance of 2.4867(1)Å. Each Cu(3)



Fig. 2. (a) Ellipsoid representation of the crescent type cluster $[SiNb_{18}O_{54}]^{14-}$ in compound **2**; (b) the 2-D framework structure via the connections between K(3) and $[SiNb_{18}O_{54}]^{14-}$; (c) 1-D chain structure running along the a axis formed by Cu(3) complex and $[SiNb_{18}O_{54}]^{14-}$; (d) The three-dimensional structure with two kinds of different channels viewing along the b axis.

complex links two neighboring $[SiNb_{18}O_{54}]^{14-}$ to form a novel 1-D chain structure running along the a axis, as depicted in Fig. 2(c). Via the connections of both K(3) and Cu(3), compound **2** shows a three-dimensional structure with two kinds of different channels viewing along the b axis (Fig. 2(d)). We can see that one of the channels is a rectangle one with the cross sectional area about $1.05 \times 0.86 \text{ nm}^2$ and the other is an S-shaped one with the cross sectional area about $1.36 \times 1.47 \text{ nm}^2$ (en ligands are omitted for clarity). Each cluster is surrounded by four S-shaped and two rectangle channels. Viewing along the a-axis, compound **2** exhibits a new rectangle channels with the cross sectional area about $1.05 \times 1.04 \text{ nm}^2$, and each polyoxoanion is surrounded by four such rectangle channels (Fig. s1).

There are also three kinds of hydrogen bonds in compound **2**. Due to the number of the dissociated water molecules is lesser than that of compound **1**, the O–H···O bonds are not as much as those included in compound **1**. And the distance ranges for N–H···O, C–H···O and O–H···O are 2.892(12)-3.356(14) Å, 3.261(16)-3.494(15) Å and 2.789(8)-2.904(16)Å respectively. Based on these synergistic interactions of all the hydrogen bonds, the PONbs and the coordination fragments are linked together, therefore increasing the stability of the 3-D framework structure in compound **2**.

3.4. Characterizations

The IR spectrum of compound **1** is shown in Fig. s2, in which the weak characteristic band centred at 929 cm⁻¹ is attributed to ν (Si-O_b-Si), the medium bands centred at 881 and 811 cm⁻¹ are ascribed to ν (Nb-O_t), and the medium bands centred at 719 and 502 cm⁻¹ are associated with ν (Nb-O_b-Nb). As for compound **2**, the weak band centred at 962 cm⁻¹ is due to ν (Si-O_c), the strong bands centred at 873 cm⁻¹ is corresponding to ν (Nb-O_t), and the strong bands centred at 713 and 506 cm⁻¹ are characteristic of ν (Nb-O_b-Nb). The absorption bands at 1683-1048 cm⁻¹ and 1607-1052 cm⁻¹ are related to vibrations of en ligands in compounds **1** and **2**, respectively.

The XRD patterns of compounds **1** and **2** are well coincident with the simulated ones, confirming the crystal phase purity (Fig. s3). The differences in the reflection intensity probably originate from the different orientations in the crystal samples of the two compounds.

3.5. Oxidation of olefins

Due to the important position of the oxidation products of olefins in synthetic chemistry, how to improve the conversion and selectivity of the olefin oxidation reaction has been the focus of scientists [63–69]. For this kind of reaction, the addition of a suitable catalyst undoubtedly is a good way to reach the purpose. POMs which are a kind of catalysts for common organic synthetic reactions, no matter in the homogeneous or heterogeneous reaction, always have a remarkable performance [38,70]. In addition, it is widely known that various copper-based cage-like coordination compounds can be employed as common catalysts in a variety of different oxidation reactions [71-74]. The combination of the copper coordination compounds and POMs perhaps can integrate the merits of both the POMs and copper complexes, leading to certain novel catalysts. In the past few years, because of the particularity of PONbs, there were only few studies about the properties of polyoxoniobates [75,76], and the few existing studies concentrated on only specific aspects, such as photocatalytic H₂ evolution activities [42,43,77]. Here, we use the compounds 1 and 2 as catalysts for the reaction of oxidation of olefins (Scheme 1), and contrastively analyse the influence of various reaction conditions on the catalytic results. The epoxidation of styrene to styrene oxide with aqueous tertbutyl hydroperoxide (TBHP 70 wt% in H₂O) using compounds 1 and 2 as the catalysts was carried out in a batch reactor. The mixture of the catalyst, styrene and solvent was heated to a certain temperature and then TBHP was injected to start the reaction. The liquid organic products were quantified by using a gas chromatograph with the area normalization method. The activity of the reaction system



Scheme 1. Main products of the selective styrene oxidation.

to oxidize styrene to styrene oxide in the absence of the catalysts was determined (Table 2, entry 1).

To achieve the optimum reaction condition, the different solvent, reaction temperature, and the dosage of the oxidant have been investigated, and all the final results are shown in Table 2. The different solvent was screened for this reaction. With ethanol as the solvent at 60 °C, the experiments have a better conversion and selectivity compared with CH₃CN as the solvent (Table 2, entries 2–5). However, when the reaction temperature increased to 70 °C, the catalytic activities sharply decreased with the conversions were even lower than 10% (Table 2, entries 8–9). We speculate that maybe the catalysts had been deactivated in such a higher temperature with the ethanol as the solvent (Table 2, entries 4, 5, 8 and 9). The reason for the deactivation of the catalysts is still elusive. We repeated the reaction in three different temperatures (60, 70, 80 °C) in CH₃CN. When the reaction temperature is 80 °C, we get the highest conversions which are for compound 1 80.8% and for compound 2 82.5% (Table 2, entries 2, 3, 6, 7, 10 and 11). Besides, when the dosage of the oxidant was increased to 2 mmol we got a better result with a higher conversion (93.1%) and a better selectivity to styrene oxide (70.4%) over compound 1, while the conversion and selectivity using 2 mmol oxidant over compound 2 were increased 93.3% and 71.1%, respectively (Table 2, entries 14 and 15). Therefore, we concluded that this POM based catalysis system are strongly dependent on the amounts of the TBHP oxidant. To better understand which is the active center of the catalysts, the Cu(Ac)₂ and Cu(Ac)₂+en were also introduced to the reaction system as catalysts. The results demonstrated that no matter the amount of the TBHP is 1 or 2 mmol, the conversions which are lower than 10% over Cu(Ac)₂+en are always worse (Table 2, entries 13 and 17). On the contrary, Cu(Ac)₂ has a better performance, which indicated that Cu perhaps make the significant contribution to the activity of the catalysts (Table 2, entries 12 and 16). The higher catalytic activity over compounds 1 and 2 whether in term of the conversion or the selectivity implies that the combination of Cu and Nb-cluster can lead to a positive synergistic catalytic improvements to the two components. Also the activity of the catalyst and the bigger molecular weight make them have a better TOF.

The homogeneity or heterogeneity of compounds 1 and 2 were confirmed by hot filtration experiments (Fig. 3). After 4h of the reaction, the catalyst was removed from the reaction system by hot filtration and the remaining filtrate was allowed to continue the reaction at the identical reaction temperature. GC analysis showed that the reaction didn't stop after the filtration of compound 1. As for compound 2, in the first 2 h, the reaction didn't stop but at the latter 2 h there was no further reaction happened. It is demonstrated that although compounds ${\bf 1}$ and ${\bf 2}$ are not completely dissolved in the reaction solution, some catalysts which can allow the reaction to continue still dissolved. And compared with compound 1, compound 2 has a lower solubility in this reaction system. The catalytic reaction is considered to be homogeneous in nature when $\Delta Filt / \Delta cat \approx 1$, where $\Delta Filt$ is the increment in olefin conversion in the time interval 4-8h for the reaction carried out using the filtered solution and Δcat is the increment in olefin conversion during the same time interval for the reaction carried out in the presence of compound 1 or 2 [78]. Here, our Δ Filt/ Δ cat equals 0.90 for compound 1 and 0.83 for

Table 2

Oxidation	of styrene	catalyzed	by	compounds	1	and 2
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Entry	Catalysts	T(°C)	Solvent	TBHP (mmol)	Conv(%)	Product selectivity (mol%)		TOF(h ⁻¹) ^c	
						So ^a	Bza ^a	Others ^a	
1	No catalyst	60	CH ₃ CN	1	Trace	-	_	_	_
2	Compound 1	60	CH ₃ CN	1	46.4	14.4	85.7	0.0	214.7
3	Compound 2	60	CH ₃ CN	1	38.0	10.1	75.8	14.1	95.0
4	Compound 1	60	EtOH	1	61.6	36.2	55.8	8.0	285.1
5	Compound 2	60	EtOH	1	65.8	28.5	61.9	9.7	164.4
6	Compound 1	70	CH ₃ CN	1	62.1	26.4	71.0	2.6	287.3
7	Compound 2	70	CH ₃ CN	1	71.6	21.0	75.0	4.0	179.0
8	Compound 1	70	EtOH	1	7.7	10.8	89.2	0.0	35 ^b 5
9	Compound 2	70	EtOH	1	7.7	11.3	88.7	2.0	19.3
10	Compound 1	80	CH ₃ CN	1	80.8	42.7	52.6	4.7	374.2
11	Compound 2	80	CH ₃ CN	1	82.5	34.2	61.0	4.8	206.3
12	$Cu(Ac)_2^b$	80	CH ₃ CN	1	62.0	28.4	65.7	5.9	15.5
13	$Cu(Ac)_2 + en^b$	80	CH ₃ CN	1	6.4	47.1	30.1	22.8	-
14	Compound 1	80	CH ₃ CN	2	93.1	70.4	23.9	5.7	431.1
15	Compound 2	80	CH ₃ CN	2	93.3	71.1	23.5	5.3	233.2
16	Cu(Ac) ₂ ^b	80	CH ₃ CN	2	82.5	48.7	45.5	5.8	20.6
17	Cu(Ac) ₂ +en ^b	80	CH ₃ CN	2	8.2	56.4	36.5	7.1	-

^a So: Styrene oxide, Bza: benzaldehyde, Others: including benzoic acid, phenylacetaldehyde.

^b $Cu(Ac)_2$: 1 mg of $Cu(Ac)_2$; $Cu(Ac)_2$ +en: $Cu(Ac)_2$ (1 mg)+en(30 μ L), the mixture was stirred for 30min and then used as catalyst.

^c TOF = turnover frequency, moles of substrate converted per mole catalyst added per hour.



Fig. 3. The results of the hot filtration test of compounds 1 (a) and 2 (b).

compound 2, such results suggest that the compounds 1 and 2 are homogeneous catalysts for the epoxidation of styrene with TBHP [78-82]. For the catalysts are not completely dissolved in the reaction, the reusability and regeneration of compound 2 are investigated (shown in Fig. 4). Under the identical reaction conditions, we did the experiment three times with 10 mg of compound 2. At the end of each reaction cycle the catalyst was recovered by simple filtration and washed with acetonitrile. After the recovered catalyst was dried in air, the catalyst was directly reused again under the same reaction condition. Each cycle experimental data reveal that the conversions are almost identical, unfortunately the selectivities are not stable. After the last cycle, we carried out the IR analysis to determine whether the catalyst has changed or not. From Fig. s4, we can see that, after the three cycles, the intensities of the IR have a few changes but the main peak positions are just the same. Combined with the above views, it is indicated that compound 2 has good recoverability and chemical stability for this catalytic reaction. The catalytic characterization results for the as-prepared and recovered catalysts are similar, and thus we can conclude that it is possible that the homogeneous contribution is due to the dissolution of a fraction of the



Fig. 4. The recycle experiments of compound 2.



Fig. 5. Electrochemical water oxidation performances of typical samples in a strong alkali solution of 1 M KOH with a traditional three-electrode system (modified CPE, Pt wire, and Ag/AgCl (3 M KCl) electrodes as the working, counter and reference electrodes, respectively. a) LSV curves of various catalysts in 1.0 M KOH without iR-compensation. b) LSV curves for per formula μ mol. C) Tafel plots derived from Fig. 5(a).

catalyst **2** rather than to its decomposition into soluble, active metal species [79].

Encouraged by the good catalytic performances of the compounds **1** and **2** for the oxidation of styrene, under the above-mentioned optimized reaction conditions the scope of substrates for this reaction system was further surveyed. As shown in Table 3, unlike the styrene oxidation catalysis, the very poor selectivities illustrate that compounds **1** and **2** did not have a good performance in the epoxidation for cyclohexene and 1-octene. However, both of the two catalysts have a relatively better activity for the cyclooctene oxidation with 60.3% conversion and 44.4% selectivity for compound **1**, and 62.7% conversion and 39.7% selectivity for compound **2**. Unfortunately, the reason for the differences among the different substrates is still elusive.

3.6. Oxygen evolution reaction

It is well known that the development and use of fossil fuels have led to many resource and environment problems [83]. So, the research and preparation of new energy have become a scientific hotspot in various disciplines for many years [84–87]. As a kind of renewable clean energy with high combustion value, the exploitation and utilization of hydrogen energy have always been the direction of chemists' efforts. However, so far, electrolysis of water is still the most effective way to obtain high purity hydrogen. In comparison with the hydrogen evolution reaction (HER), another half-reaction, oxygen evolution reaction (OER), more determines the efficiency of water electrolysis, it can be said that the higher efficiency of oxygen evolution reaction we get the better speed and ability of water electrolysis we gain [88–91]. Because of their outstanding chemical properties and lower cost, POMs have also been used as catalysts for oxygen evolution reaction [52–54], but until now there is not a systematic study for heteropolyoxoniobates(HPONbs) as a catalyst for OER. Here, we take the compounds 1 and 2 as the catalysts for the OER process. Without the IR-compensation in a strong alkali solution of 1 M KOH solution, the test was taken with a traditional three-electrode system (modified CPE, Pt wire, and Ag/AgCl (3 M KCl) electrodes as the working, the counter and the reference electrodes, respectively). Their linear sweep voltammetry (LSV) curves at the scan rate of 1 mV s⁻¹ are shown in Fig. 5, the current densities showed a rapid increase deviating from the flat response of the pure CP, indicating the appearance of catalytic currents. As we can see, compound 1 has a superior performance compared with compound **2**. The overpotential values at 1 mA/cm^2 and 10 mA/cm² for compound 1 are 222 mV and 533 mV, respectively. And at the same current density of 1 mA/cm², compound 2 has a higher overpotential of 308 mV. Cu(Ac)₂ exhibits a comparable performance to that of compound 1 with the overpotential of 542 mV at 10 mA/cm^2 . It is worth mentioning that the comparisons between compound 1 and Cu(Ac)₂ by weight are unfair to the HPONbs catalysts. At the same weight, the number of active sites in the $Cu(Ac)_2$ electrode is about one order of magnitude higher due to its lower molecular weight and higher density of active sites. If we normalize the current density data taking into account the total number of Cu centers, the activity of compound 1 is remarkably better than that of Cu(Ac)₂ (Fig. 5(b)). Beyond that, the lower slope of corresponding Tafel plots which were drawn using the LSV data for compound 1 (234 mV·dec⁻¹) also indicates that it has a better activity for water oxidation compared with compound 2 (314 mV·dec⁻¹) (Fig. 5(c)). The electrochemical impedance spectroscopy (EIS) test was always seen as a strong evidence for the performance of OER. We can see compound 1 has a lower resistance (Fig. s5), indicating a good conductivity that is conducive to electron transfer which is consistent with the Tafel slope, too. We speculated that the chain structure of cluster might give compound 1 a better electrical conductivity. As for the stability experiment, both the two compounds have a significant current loss in

Table 3

	Catalvtic	oxidation	of	different	olefin	substrates. ^a	
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Entry	Substrate	Catalyst	Product	Conv./%	Sel./%
1		1 2		91.7 90.3	1.8 1.3
2	$\tilde{\bigcirc}$	1 2		60.3 62.9	44.4 39.7
3	C6H13CH CH2	1 2	C6H13CH CH2	69.4 71.1	1.8 1.5

^a Reaction condition: substrate (1 mmol), catalyst (2 mg, 0.27 µmol for compound 1, 0.50 µmol mmol for compound 2), TBHP (2 mmol), CH₃CN (2 mL), t = 8 h.

the first 1 h (Fig. s6), however after that, compound 2 get a better stability result and the 3D structure of compound 2 may play an important role for its relative stability.

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4. Conclusions

Two new polyoxoniobosilicates compounds based on {Si₄Nb₁₆} or {SiNb18} and copper-en complexes have been synthesized and characterized. Compound 1 is structurally similar to the compound reported by Nyman et al. [44]. However, detailed analysis found that the compound 1 and the Nyman's compound have some significant differences. Compound **2** is a novel 3-D framework structure constructed from $\{SiNb_{18}\}$, copper complexes and potassium ions via both strong Cu-O and K-O interactions. The experiment results showed that as the catalysts, both of the two compounds have activities for the oxidation of styrene and oxygen evolution reaction (OER). And for the oxidation of styrene test, compounds 1 (93.1% conversion and 70.4% selectivity to styrene oxide) and 2 (93.3% conversion and 71.1% selectivity to styrene oxide) exhibit a similar performance; however, as for the OER, compound 1 (10 mAcm⁻² at 533 mV) shows an obvious superiority compared with compound **2**. And for this result we speculated that the special crystal structure of compound 1 may create a better conductivity which makes a better activity for the OER. On the basis of the current works, we hope to design and synthesize more PONbs with better catalytic performances or some composites with PONbs supported on substrates like graphene in the future work.

CRediT authorship contribution statement

Ting-Ting Zhang: Writing - original draft, Synthesizing the compounds, do all the experiments of the characterizations and catalysis. Zi-Qiu Zhao: Some experiments of the characterizations and catalysis. Ge Tian: The experiments of the catalysis. Xiao-Bing Cui: Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.jssc.2021.122029.

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