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Polyoxotungstates incorporated organophosphonate and nickel: synthesis, characterization and efficient catalysis for epoxidation of allylic alcohols

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Abstract: Three new sandwich-type organophosphonate-functionalized polyoxotungstate clusters, $[{Ni(H_2O)_5}_{X}(AsW_6O_{21})_{Ni}(OOCCH_2NCH_2PO_3)_2]_3]$ (x = 0 (Ni1); 1 (Ni2 and Ni3)), were successfully isolated via executing the "top-down" synthetic strategy. Compounds (Ni1-Ni3) were characterized by single crystal X-ray analysis, X-ray powder diffraction (XRPD), IR spectroscopy, UV-vis spectroscopy, and thermogravimetric analyses (TGA). Magnetic properties provide evidence for antiferromagnetic coupling in Ni2 and Ni3 whereas ferromagnetic interaction in Ni1. Catalytic studies of three polyoxotungstates for the oxidation of allylic alcohols to epoxides have been investigated in water with H₂O₂ as the oxidant, which exhibits efficient catalytic performance with excellent conversion and high selectivity at room temperature.

Introduction

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Polyoxometalates (POMs), as the metal-oxide nanoclusters exhibit controllable and diversiform structures, along with high thermal and oxidative stability. Nowadays, the consistent use of POMs is mainly manifested due to their remarkable electronic behavior, magnetism and Brønsted acidity, thus expanding them in catalysis,1 magnetism,² biology³ and in pharmacy.⁴ Moreover, the nucleophilic surface-oxygen atoms facilitates POMs to be used as multidentate inorganic ligands to coordinate metal centers⁵ (transition metals (TMs) or lanthanide ions) but could also functionalized with organic groups, which is an effective strategy in obtaining POM-based multifunctional materials.⁶ Meanwhile, organophosphorus, a kind of multifunctional ligands, possesses high thermostability and robust resistivity against hydrolysis, which has exhibited wide applications ranging from catalysis to medicine.⁷ Moreover, organophosphonatebased POMs derivatives occupy an important place in POMs chemistry due to their splendid properties.⁸ Thereby, inorganic (TMs) and organic (phosphonates) functionalized POMs could be used in improving the physicochemical phenomena in catalysis.⁹ It is worth noting that there are still relatively limited studies have been performed on organophosphonate-functionalized polyoxotungstates

(POTs). in contrast to the abundant derivatives of polyoxomolybdates¹⁰ and polyoxovanadates.¹¹ In fact, the first organophosphonate-based example of POTs is Pope's [(O₃PCH₂PO₃)₄W₁₂O₃₆]¹⁶⁻ reported in 1994,¹² thereafter, only several literatures contributed towards the development of organophosphonate-decorated POTs.13 Until 2012, TMs was firstly introduced into organophosphonate-based POTs by Mialane and coof workers for the preparation [{(B-α-PW₉O₃₄)Co₃(OH)(H₂O)₂(O₃PC(O)(C₃H₆NH₃)PO₃)}₂Co]^{14-.14} Afterwards, they synthesized organophosphonate-based POTs containing nickel 2013.¹⁵ Later on, our group reported, atoms in $[H_4\{(AsW_9O_{33})Zn(H_2O)W_5O_{11}(N(CH_2PO_3)_3)\}_2(\mu_2 - O)_2]^{10-} \ \, \text{in the year} \\$ 2014, which contains different geometry of а $[{Zn(H_2O)W_5O_{19}(N(CH_2PO_3)_3)}]^{12-}$ cluster in a chiral conformation which was also used as an efficient catalyst for olefin epoxidation.¹⁶

Hence, it is significant to construct original organophosphates functionalized POTs, which bear novel properties but also, can contribute significantly to the development of POMs chemistry. However, compared the rapid development to of organophosphonate-based polyoxomolybdates, there were few POTs with reports which deals on functionalized organophosphonates which might be attributed to lower reactivity amongst organophosphorus and POTs. In order to overcome this obstacle, the following strategies were adopted: 1) contrary to the traditional "bottom-up" condensation reactions, "top-down" approach was used to produce the active species in order to improve the reactivity between POTs and organophosphorus.¹⁷ 2) Organophosphorus equipped nitrogen enhance the coordination ability.

Recently, considerable efforts have been aimed towards the epoxidation of allylic alcohols as the products have been applied as raw materials for epoxy resins, building blocks for biologically

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Electronic Supplementary Information (ESI) available: The infrared spectrum of the three POMs (Figure S1); The XRD of the three POMs (Figure S2); The structure of the POMs (Figure S3); The plots for and χ M-1 vs T between 1.8 K and 300 K for three POMs (Figure S4); The TGA curves of Ni1, Ni2 and Ni3 (Figure S5); The Vis spectra of Ni1, Ni2 and Ni3 (Figure S6); The comparison of solution 1H NMR spectra of the three POMs and glyphosate (Figure S7). See DOI: 10.1039/x00x0000x

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important compounds and chiral molecules.¹⁸ Thus, substantial researches in the design and construction of splendid catalytic system for the rapid transformation from allylic alcohols to epoxides have been gaining much attention, where POTs appears with good catalytic performance in the aforementioned process.¹⁹ Furthermore, the combination of TMs and glyphosate into POTs may possess wonderful catalysis for the epoxidation, which is also in consistent with the synthetic target. Moreover, the development of efficient and practical epoxidation technology mainly employs aqueous H₂O₂ as the oxidant because of its high contents of active oxygen species and co-production of eco-friendly water.²⁰

Herein, $K_{14}[As_2W_{19}O_{67}(H_2O)]$ (As₂W₁₉) as an active precursor was chosen to be disassembled to generate peculiar and active building blocks. Meanwhile, glyphosate, as a kind of the organophosphorus ligands in this synthetic system, have one phosphoryl and carboxyl group on two terminals along with one center nitrogen atom, which could be used to increase the possible combination of TMs and POMs. As expected, three new sandwich-type TMs-containing POTs functionalized obtained: glyphosate were K₁₄H₁₀[(AsW₆O₂₁)₂{Ni(OOCCH₂NCH₂PO₃)₂}₃]·25H₂O (Ni1), $K_8H_{14}[{Ni(H_2O)_5}(AsW_6O_{21})_2{Ni(OOCCH_2NCH_2PO_3)_2}_3] \cdot 20H_2O$ (Ni2) and Cs2K5H15[{Ni(H2O)5}(AsW6O21)2{Ni(OOCCH2NCH2PO3)2}3]·18H2O (Ni3), where TMs and organophosphorus were incorporated into POTs successfully. Beside this, the catalytic process was executed with H_2O_2 as oxidant and water as solvent which limits the expensive environmentally-unacceptable oxidants and hazardous organic solvents. Notably, the synthetic POTs have shown superior catalytic performance for epoxidation of allylic alcohols at room temperature in an economic and eco-friendly approach.

DOI: 10.1039/C8DT02590H All the reagents were of analytical grade and obtained from purification. commercial sources without further K₁₄[As₂W₁₉O₆₇(H₂O)] was prepared using literature methods²¹ and characterized by IR spectroscopy. All of the allylic alcohols were purchased from J&K Chemical. Hydrogen peroxide was obtained from Deen Reagent.

Synthesis of K₁₄H₁₀[(AsW₆O₂₁)₂{Ni(OOCCH₂NCH₂PO₃)₂}]·25H₂O (Ni1)

K₁₄[As₂W₁₉O₆₇(H₂O)] (0.66 g) and glypho e were dissolved in 10 mL of deionized water and NiCl₂·6H₂ (0.24 g) was added after 10 minutes stirred solution. Follow by the addition of KCl (0.1 g) into the above mixture, the pH as adjusted to 6 by 3M KOH. Afterwards, the green clear solu on was stirred in 80 °C for 1.5 h and then the precipitate was moved by filtration. The blue block shape crystals of Ni1 were ollected after about three weeks. Yield: 0.42g (23.9% ba d on NiCl₂·6H₂O). Elemental analysis (%) calcd for Ni1: C, 5; H, 1.61; N, 1.61; Ni, 3.38; P, 3.57; W, 42.41; As, 2.88; K, 10 2. Found: C, 3.98; H, 1.84; N, 1.73; Ni, 3.28; P, 3.82; W, 42.2 As, 2.23; K, 10.41. Selected IR (KBr, cm⁻¹; b, broad; s, st ıg; m, medium; w, weak;): 3385 (b), 3256 (w), 2948 (w), 15 (s), 1394 (m), 1260 (w), 1214 (w), 1110 (s), 998(w), 922 (s), '6 (s), 797 (m), 693 (s), 609 (w), 518 (w).

Synthesis of

Ni2

 $C_{18}H_{88}N_6O_{97}P_6As_2W_{12}Ni_4K_8$

5030.20

3)2}3]·20H2O (Ni2) K₈H₁₄[{Ni(H₂O)₅}(AsW₆O₂₁)₂{Ni(OOCCH₂NCH₂

The preparation of Ni2 (light block shape cry lls) is quite similar to Ni1, but with RbCl (0.1 g) instead of KCl and pH was adjusted

Results and discussion

Empirical formula

Table 1 Crystallographic data and structure refinement parameters for Ni1, Ni2 and Ni3.

Ni1

As2Ni3O97P6W12C18H84N6K14

γ[°] V[ų] Ζ

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Formula weight 5202.06 P321 C2/cSpace group са monoclinic orth ombic Crystal system trigonal 22.6407(11) 23.181(6) a [Å] 26 '0(2) b [Å] 22.6407(11) 18.465(5) 29 64(3) c [Å] 19.7106(10) 34.868(12) 36 9(3) α [°] 90 90 0 β [°] 90 105.887(5) 0 120 90 0 8750.0(10) 14356(7) 28 96(4) 3 4 8 ρ_{calcd} [g cm⁻³] 2.918 2.284 2.355 μ [mm⁻¹] 13.507 10.927 11.346 R_{int} 0.0581 0.1038 0.1077 -27 ≤ h ≤ 25, -27 ≤ h ≤ 27, -31 ≤ h ≤ 31, -27 ≤ k ≤ 23, -18 ≤ k ≤ 22, $-35 \leq k \leq 29$ Limiting indices -23 ≤ | ≤ 23 -31 ≤ | ≤ 41 -43 ≤ | ≤ 43 **Reflections collected** 45446 145052 35144 F (000) 7008 9040 18520 GOF on F² 1.063 1.039 1 033 R1, wR2 ($l > 2\sigma(l)$) 0.0418, 0.1018 0.0882, 0.2422 0.0691, 0.1679 R1, wR2 (all data) 0.0505, 0.1067 0.1275, 0.2776 0.1242, 0.2110

and glyphosate were dissol and NiCl ₂ · $6H_2O$ (0.24 g) was tion. Followed by the addit ture, the pH was adjusted t en clear solution was stirred cipitate was removed by filth of Ni1 were collected after (23.9% based on NiCl ₂ ·· for Ni1 : C, 4.15; H, 1.61; N s, 2.88; K, 10.52. Found: C, 3 82; W, 42.25; As, 2.23; K, proad; s, strong; m, mediu 948 (w), 1595 (s), 1394 (m) w), 922 (s), 876 (s), 797 (m
00CCH₂NCH₂PO₃)₂}₃]·20H₂O (N
ock shape crystals) is quite sim d of KCI and the pH was adjus
Ni3
C ₁₈ H ₈₅ N ₆ O ₉₅ P ₆ Ni₄As ₂ W ₁₂ K ₅ Cs ₂ 5143.69 <i>Pbca</i>
orthorhombic
26.670(2)
29.464(3)
20,219(3) 30,219(3)
90
90
28696(4)
20030(4)

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Fig. 1. (a) Schematic presentation of synthesis of the anion Ni1; (b) The polyhedral/ball-and-stick representation of the polyanionic skeleton of Ni1; (c) The ball-and-stick representation of the building blocks; (d) The planform of the three Ni atoms incorporated with glyphosate ligands; (e) the coordination mode between one Ni atom and two ligands. (WO₆/W: cyan, P: yellow, Ni: green, C: black, N: blue, O: red.)

to 5.8. Yield: 0.39g (30.5% based on NiCl₂·6H₂O). Elemental analysis (%) calcd for Ni2: C, 4.29; H, 1.75; N, 1.67; Ni, 4.67; P, 3.70; W, 43.86; As, 2.98; K, 6.22. Found: C, 4.15; H, 1.83; N, 1.51; Ni, 4.52; P, 3.97; W, 44.68; As, 3.23; K, 6.28. Selected IR: 3410 (b), 3253 (w), 2945 (w), 1695 (s), 1391 (m), 1331 (w), 1257 (w), 1216 (w), 1110 (s), 998 (w), 926 (s), 876 (s), 793 (m), 693(s), 605 (w), 513 (m).

Synthesis of

$Cs_2K_5H_{15}[{Ni(H_2O)_5}(AsW_6O_{21})_2{Ni(OOCCH_2NCH_2PO_3)_2}_3] \cdot 18H_2O$ (Ni3)

The preparation of **Ni3** (light block shape crystals) is similar to **Ni1**, but with CsCl (0.1 g) instead of KCl and the pH was adjusted to 6.5. Yield: 0.45g (34.5% based on NiCl₂·6H₂O). Elemental analysis (%) calcd for **Ni3**: C, 4.20; H, 1.65; N, 1.63; Ni, 4.56; P, 3.62; W, 42.89; As, 2.91; K, 3.80; Cs, 5.17. Found: C, 4.02; H, 1.72; N, 1.89; Ni, 4.43; P, 3.85; W, 43.58; As, 2.96; K, 3.69; Cs, 5.22. Selected IR: 3400 (b), 3248 (w), 2951 (w), 1595 (s), 1391 (m), 1333 (w), 1251 (w), 1214 (w), 1101 (m), 998 (m), 928 (s), 879 (s), 801 (m), 740(s), 693 (s), 604 (w), 517 (m).

Characterization

Elemental analyses of C, H, and N were performed with an Elementar Vario Elcube CHNS analyzer (Perkin-Elmer, Waltham, MA, USA). Elemental analysis for W, Ni and P were performed with a Perkin Eimer Optima 2100 DV (Perkin-Elmer, Waltham, MA, USA) inductively coupled plasma optical emission spectrometer. IR spectra were recorded on a Bruker VERTEX 70 IR spectrometer (Nicolet, Madison, WI, USA) (using KBr pellets) in the range of 4000–400 cm⁻¹. X-ray powder diffraction (XRPD) data were recorded on a Bruker AXS D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with Cu K α radiation in the angular range 2 θ = 5–45° at 293 K. TG analysis was measured on NETZSCH STA449F5/QMS403D instrument (Mettler-Toledo, Schwerzenbach, Switzerland) with a heating rate of 10 °C min⁻¹ from 25 °C to 870 °C in N₂ flow.

The procedure of the catalysis for the epoxidation of allylic alcohols

The allylic alcohols (5 mmol), H_2O_2 (5 mmol) catalyst (0.2 mol%) and water (1 ml) were added into a tube at room temperature. Afterwards, the mixture was stirred at the prescribed conditions on the parallel reactor. The product carried on qualitative detection by GC-MS and the yield was monitored by GC with dodecane as internal standard.

X-ray crystallographic determination

Crystallographic study for **Ni1**, **Ni2**, and **Ni3** were performed at 296(2) K on a Bruker Apex-II CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Intensity data were corrected for Lorentz and polarization effects as well as for multi-scan absorption by an applied multiscan absorption correction SADABS program. Direct methods (SHELXS97) were used to solve their structures, and

ARTICLE

Journal Name

the heavy atoms were located by full matrix least-squares refinements on F2 and Fourier syntheses using the SHELXS-1997 program package. In the final refinement cycles, the W, As, Ni, and P atoms were refined anisotropically; the O, C and N atoms were refined isotropically. The lattice water molecules were determined by the TGA results. The hydrogen atoms of organic groups were fixed in calculated positions and then refined using a riding model. Collected crystal data and structure refinement parameters for Ni1, Ni2, and Ni3 are given in Table 1.

Structure description

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X-ray analyses reveal that compounds Ni1, Ni2 and Ni3 crystallize in the trigonal P321, monoclinic C2/c and orthorhombic space group Pbca, respectively. The polyanions (Ni2 and Ni3) exhibit similar framework to Ni1 except one extra disordered Ni atoms. Herein, the crystal description of only Ni1 is described in detail. The structural units of Ni1 contains 14 potassium cations, 10 hydrogen 25 water molecules and cations. one $[(AsW_6O_{21})_2[Ni(OOCCH_2NCH_2PO_3)_2]_3]^{24-}$. As shown in Fig. 1b, the polyoxoanion in Ni1 consists of two {AsW₆O₂₁} building blocks, three nickels and six glyphosates. To be specific, the same building blocks $\{AsW_6O_{21}\}$ in three polyoxoanions as shown in Fig. 1c, mainly generated by the connection of one As atom with three {W2O10} units which are in vertex-sharing, formed by the side-sharing of two {WO₆} octahedrons. Additionally, each nickel atom is octahedrally coordinated by two nitrogen atoms and four oxygen atoms of two glyphosate molecules, respectively, which constructs the framework of {Ni(OOCCH₂NCH₂PO₃)₂} subunits (Fig. 1e). Afterwards, there are three {Ni(OOCCH₂NCH₂PO₃)₂} subunits, sandwiched by two $\{AsW_6O_{21}\}$ building blocks via the six $P-O_w$ linkers generating polyoxoanions in Ni1. Notably, three nickel atoms in {Ni(OOCCH₂NCH₂PO₃)₂} subunits are located at the three vertexes of one equilateral triangle (Fig. 1d), respectively, where the same distance among them is 7.553 Å. For Ni2 and Ni3, there is one {Ni(H₂O)₅} unit (Fig. S1h and S1i, respectively) filled in the triangle consisted of three nickel atoms in Fig. S1b. Moreover, the



disordered nickel atom in the {Ni(H₂O)₅} unit has existed in two locations which have been shown in Fig.^DS1b¹⁰ Mitterestingly,⁵ He disordered Ni atom bonded with the above nickel atoms in the triangle, which has made an obvious effect on their structures. As it has been shown in Fig. S1e, the triangles in **Ni2** have transformed to isosceles triangles, where the length of two same sides is 7.617 Å and the length of the longer side is 7.746 Å. As to **Ni3**, three sides in the triangle are not equivalent due to the different occupancy of the nickel at two sites, which are in the length of 7.755 Å, 7.565 Å

Magnetic Properties

and 7.768 Å (Fig. S1f).

Variable-temperature magnetic susceptibilities of the three POTs have been investigated under an applied direct current (dc) field of 1000 Oe from 300 to 1.8 K. As shown in Fig. 2, the $\chi_M T$ value of 3.12 cm³ K mol⁻¹ at 300 K for Ni1 is in good agreement with that expected for three non-interacting Ni^{II} ions of 3.00 cm³ K mol⁻¹ (S = 1, g = 2). Upon cooling, the $\chi_M T$ value of Ni1 increases to a maximum of 3.75 cm³ K mol⁻¹ at 14 K, and then decreases to the minimum of 2.26 cm³ K mol⁻¹ at 1.8 K. Ni1 exhibits Curie–Weiss behavior in the temperature range of 110-300 K, with a Curie constant of C = 3.23 cm³ K mol⁻¹ and Weiss constant of Θ = 3.68 K (Fig. S4a and S4d), which has shown that the ferromagnetic interaction exists in Ni1. As to Ni2 and Ni3, the value of χ_{MT} at 300 K is 4.69 cm³ K mol⁻¹ for Ni2 and 4.24 cm³ K mol⁻¹ for Ni3, which is in good consistent with that for four non-interacting Ni II ions of 4.00 cm³ K mol⁻¹. However, the $\chi_M T$ value undergoes a gradual decrease while the temperature is lowered, which is different from Ni1. Afterwards, there is a sharp reduction in the temperature range of 16–2 K and the χ_{MT} value reaches a minimum of 2.24 cm³ K mol⁻¹ at 1.8 K. Besides, the plots of $1/\chi_{M}$ versus T for Ni2 and Ni3 conform to the Curie-Weiss law (Ni2: C = 4.63 cm³Kmol⁻¹, Θ = -2.27 K; Ni3: C = 4.18 cm³Kmol⁻¹, Θ = –2.39 K (Fig. S4b, S4c and S4e)), which indicated that there are antiferromagnetic couplings in Ni2 and Ni3.

Solution ³¹P NMR Studies

The solution ^{31}P NMR spectra (D₂O) of Ni1, Ni2, Ni3 and raw materials have been investigated at room temperature. As



Fig 2. (a) the comparison of solution ^{31}P NMR spectra of POMs, raw materials and the mixture of NiCl₂ and H₂O₂; (b) the solution ^{31}P NMR spectra of Ni1 versus different time.

4 | J. Name., 2012, 00, 1-3

shown in Fig. 3a, the ³¹P NMR spectra have shown that there is only one signal in each POMs with slight difference in chemical shifts, which indicates that all P atoms are magnetically equivalent phosphorus corresponding to the symmetrical framework. Moreover, the comparison of the ³¹P NMR chemical shifts of glyphosate and the mixture (As₂W₁₉, NiCl₂ and glyphosate) shows an obvious difference from the synthetic POMs, as the peaks appear wider and weaker because of the paramagnetic centers (Ni $^{2+}$). Besides, a small skewing in the ¹H NMR spectra between the synthetic POMs and glyphosate has been observed in Fig. S7, which indicated bonded glyphosates to the nickel centers in In order to detect the stability of Ni1, the ¹H NMR study for the mixture (Ni1 and H_2O_2) and Ni1 in aqueous solution versus time have been performed. The results showed that the chemical shift has changed when H_2O_2 was added; however, it is different from raw materials and glyphosate. As it has shown in Fig. 3b, the ³¹P NMR spectra of Ni1 was tested versus time and the results have shown that there was no apparent change for Ni1 in aqueous solution even after 11 hours.

UV/Vis spectra

In order to investigate the UV-vis spectra behaviors of the POMs in solution, systematic studies of UV-vis spectra for time-dependent and the comparison between the obtained POMs and raw materials were monitored. As shown in Fig. 4, the UV spectra of three POMs are monitored in the range of 190-400 nm. The strong peak at 195 nm is assigned to the charge transfer transition of $p\pi$ -d π from O_t to W, while the peak at 265 nm corresponds to the charge transfer transition of $p\pi\text{-}d\pi$ from O_b and O_c to W. As the results of the comparison showed in Fig. 4a, although the UV spectra of the samples containing W also showed the peak at 265 nm, there were obvious distinction between raw materials and synthetic POTs at the range of 190-220 nm.²² Additionally, Fig. 4b-d have exhibited that the UV absorption peaks of three compounds are almost unchanged in principle, which proves that they can exist stably in aqueous solution for at least ten hours at room temperature. In the visible region, a broad peak at around 630 nm is observable in Fig. S6,



Fig. 4. (a) The compared UV spectra of different samples (L: glyphosate, mixture: As₂W₁₉ + NiCl₂ + glyphosate); The UV-vis spectra of Ni1 (b), Ni2 (c) and Ni3 (d) for time-dependent.

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which is assigned to electronic transitions which could be assigned for either d-d (${}^{3}T_{1} \rightarrow {}^{3}T_{2}$) or LMCT in character 2310.1039/C8DT02590H

Catalysis

Optimization of the catalyst

Initially, the epoxidation of 3-Methyl-2-buten-1-ol as the model reaction was performed with different catalysts in order to select the optimal catalyst to be employed in this system. As shown in Table 2, the reaction hardly took place in the absence of the catalyst (entry 1, Table 2). However, there is huge promotion once adding the POMs into this reaction. Besides, the precursors were also investigated in the same conditions and the results have shown that no efficient catalysis for the process could be detected. Obviously, Ni1 has exhibited the best catalytic performance (98% conversion and 96% selectivity, entry 2, Table 2) among three POMs, which could induce itself to be used for the following studies.

Influence of different factors on the process

To our best knowledge, reaction temperature, dosage of catalyst, loading of H₂O₂, temperature and solvents all play critical roles in this transformation. On the basis of the above results, Ni1 was employed for the transformation to investigate the effect of different factors. As shown in Fig. 5a, the influence of dosage of catalyst was studied from 0.1 to 0.3 mol%. And the results have shown that the conversion and selectivity of the reaction have been significantly improved when the dosage of catalyst was enhanced from 0.1 to 0.20 mol%. However, there was not obvious increase in conversion and selectivity when the amount of catalyst was from 0.20 to 0.25 mol% but a little decrease in selectivity from 0.25 to 0.30 mol%. Hence, 0.20 mol% consider as optimal dosage of catalyst in the reactions. For the effective H₂O₂ loading, the ratio (H₂O₂: substrate) of 0.8, 1, 1.2 and 1.6 have been applied (Fig. 5b), which have shown the enhancement from 0.8 to 1 in their catalytic activity a reduction in selectivity were noticed with the continued increase in H₂O₂ amount. Considering the temperature effect on catalytic process, an obvious



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Table 2.

The epoxidation of methyl-2-buten-1-ol was performed with different catalysts.



Entry	Cat.	Conv. ^b (%)	Sel. (%)	
1 ^a		2	80	
2	Ni1	97.5	96	
3	Ni2	94.5	89	
4	Ni3	94.8	90.5	
5	glyphosate	4.3	77.8	
6	NiCl ₂	3.3	86	
7	As ₂ W ₁₉	53.4	53.6	
8	Mixture	67.6	82.7	

^a Reaction conditions: 3-methyl-2-buten-1-ol (5 mmol), H₂O₂ (5 mmol), catalyst (0.2 mol%) H₂O (1 mL), 25 °C; ^b All of the products were identified by GC–MS spectra. The results refer to GC spectra based on dodecane as internal standard.

melioration with the rise of temperature were observed till it reaches to 25 °C (Fig. 5c). As the increase of temperature went on, the conversion and selectivity of the reaction would decline. Besides, solvents also have an important effect on this reaction, consequently, several contrast experiments were performed in various solvents. As it has been shown in Fig. 5d, the reaction executed in acetone could obtain better catalysis than in alcohol and acetonitrile, which may be influenced by the polarity of solvent. Besides, the reaction in eco-friendly water exhibited the best catalytic performance amongst the other solvents. Unfortunately, the results of solution ³¹P NMR spectra have shown that Ni1 will change when H₂O₂ is added but the contrast experiments implied that the raw materials presented little catalytic performance, which hinted that Ni1 may have been transformed into other active species in the process to benefit this catalysis.

Scope of substrate

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Encouraged by the above results, the epoxidation of various allylic alcohols (2-methyl-2-propen-1-ol, trans-2-hexen-1-ol and crotyl alcohol) with equivalence of aqueous H_2O_2 was carried out in this



catalytic system. As can be seen from Fig. 6, 3-Methyl-2-buten-1-ol afforded the best activity: 98% epoxide conversion and 96% selectivity in one hour, which may benefit from the higher nucleophilicity of the C=C. While the trans-2-hexen-1-ol is less reactive: only 63% conversion and 96% selectivity could be detected after 6 hours. In addition, 2-methyl-2-propen-1-ol and Crotyl alcohol have shown 100% selectivity at 99.2% conversion and 99.5% selectivity at 98% conversion, respectively, which were obtained by prolonging the reaction time to 6 h. Therefore, the results suggested that **Ni1** have shown splendid catalysis for the epoxidation of allylic alcohols.

Conclusion

In summary, а plausible route to introduce organophosphonate into POTs have been accomplished via the disassembly of the [As₂W₁₉O₆₇]¹⁴⁻ into active species and glyphosate (containing N atom) as the ligand to improve the reactivity among organophosphonate, TMs and POTs. As sandwich-type expected. three organophosphonatefunctionalized POTs incorporated TMs were synthesized successfully by self-assembly, which is of utmost importance in POM chemistry. Interestingly, the magnetic properties of three POMs have been investigated systematically: antiferromagnetic coupling in Ni2 and Ni3 but the ferromagnetic interaction in Ni1. Notably, the three POMs all exhibited efficient catalysis for the transformation from allylic alcohols to epoxides at room temperature. In addition, water as solvent and H₂O₂ as oxidant have prevented environment from the damage of nocuous organic solvents and oxidants, which is advocated in the green process of chemical production.

Conflicts of interest

There are no conflicts of interest to declare.

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Polyoxotungstates incorporated organophosphonate and nickel:

synthesis, characterization and efficient catalysis for epoxidation of

allylic alcohols

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"Top-down" synthetic strategy was performed via $K_{14}[As_2W_{19}O_{67}(H_2O)]$ as precursor to be disassemble to obtain active building blocks which can incorporate nickle and glyphosate to overcome the trouble in the synthesis of organophosate-based POTs. Moreover, the synthetic POTs exhibited superior catalysis for the epoxidation of allylic alcohols in water with H_2O_2 as oxidant under room temperature, which prevented environment from the damage of nocuous organic solvents and oxidants.