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Regulating catalytic activity of multi-Ru-bridged polyoxometalate based on active sites differential environment with six-coordinate geometry and five-coordinate geometry transition

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Synthesis

Mixed-metal-bridged POMs for catalysis. Eco-friendly, clean, and renewable catalytic oxidation has been treated as one kind of important substitute of catalytic industry, thus considerable attention is directed towards searching effective and sustainable ways for the oxidation of substrate.¹ Coincidently, POMs due to all-inorganic nature and robust structural framework exhibit excellent solution, thermal and redox stability, making them attractive catalysts or catalytic components. For instance, some Keggin-type heteropolytungstates including $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, $BW_{12}O_{40}^{5-}$ and $GeW_{12}O_{40}^{4-}$ have proven to be homogeneous catalysts in acidic aqueous solutions.² However, traditional POM architypes often need severe reaction conditions such as high temperatures/pressure and specified solvent, which extremely limits the improvement of catalytic efficiency of oxidation.³ On this foundation, room temperture and solvent-free reaction using novel mixed-metal-bridged POMs catalysts is believed to be a promising approach to produce target product from substrate on a large scale and has attracted much attention in the past few decades.⁴

The introduction of other transition metal into mixed-metal-bridged POMs will not only improve the stability of structures but also bring some new catalyst properties.⁵ However, lots of noble metalscontaining POMs exhibit higher efficiency on the selective oxidation reactions.⁶ In particular, many lacunary Keggin-type polyanions, incorporating several noble metals, have been subjected to a vast number of studies for their catalytic activity.⁷ Among the multitudinous noble metals-containing POMs structural motifs, Ru-bridged Keggin-type polyanions endow POMs with unique properties due to the redox and catalytic properties of Ru atoms.⁸ In this regard, Ru-bridged Keggin-type POMs have already proven to be an effective strategy for maximize the superiority of POMs and Ru.⁹ Previous studies have indicated that Ru-bridged Keggin-type POMs are excellent catalysts for the oxidation of organic substrates.¹⁰ For instance, the mono-Ru-bridged silicotungstate [SiW₁₁O₃₉Ru^{III}(H₂O)]⁵⁻, first reported by Neumann, RuCl₃ successfully react with the lacunary silicotungustate in organic medium, as a heterogeneous catalyst for the oxidation of a wide range of alcohols using 1 atm of molecular oxygen as the sole oxidant.¹¹ Subsequently, Liu and coworkers reported a Ru-bridged Keggin-type heteropolyoxometalate, $[RuCl_4(L)_2]_3PW_{12}O_{40}$ (L = 1-butyl-2-diphenylphosphino-3-methylimidazolium), which acts as an efficient catalyst for the aerobic oxidation of benzyl alcohol free of base and nitroxyl radical.12

Introducing active site for catalysis. Designing POM catalysts with rich active sites by engineering of polyanion structures is an effective method to enhance their catalytic activity. Many strategies for introducing active sites, such as heteroatom doping and metal-exchanged, which can enhance the performance and generate novel structures, have been developed to solve the defect problem in the POMs area. A new strategy was developed to introduce active sites Ru³⁺ into the pores of POM precursors, thereby exposing more active sites.¹³ Simultaneously, the stability of polyanions can be significantly increased via the immobilization atoms of Ru into functional anions form multi-Ru-bridged POMs. Whereas, controlled exposure-area of active sites is a severe challenge in a nanostructured POM compounds. The development of efficient catalysts with precisely modulated active sites is crucial for exploring the reaction mechanism and promoting the oxidation process. Herein, we present the isolated Ru atom-decorated POMs with precisely engineered active sites for enhanced catalytic activity. Experimental investigations showed that the introduction of Ru active sites could improve the acid resistance, alkali resistance and high temperature resistance and the elimination of coordinate water molecules could improve catalytic activity. This study demonstrates the validity of exposure-area

control of active sites in POM-based catalysts, which could also be extended to the design of highly efficient catalysts for other energy-related processes.

Supplementary Structural Figures



Fig. S1 a) Combined polyhedral/ball-and-stick representation of As_4W_{40} with an indication of the S1 and S2 binding sites. b) Combined polyhedral/ball-and-stick representation of the title polyanion **1**. Color code: O (red), Ru (yellow), As (pink), WO₆ octahedra (sea green) and bridging groups WO₆ octahedron (sky blue).



Fig. S2 a) Combined polyhedral/ball-and-stick representation of polyanion for $[Pd_2Na_2KAs_4W_{40}O_{140}(H_2O)]^{21-}$. b) Combined polyhedral/ball-and-stick representation of polyanion for $[As_4W_{40}O_{140}\{Ru_2(CH_3COO)\}_2]^{14-}$. Color code: C (black), O (red), Ru (yellow), As (pink), Pd (orange), WO₆ octahedra (sea green) and bridging group WO₆ octahedron (sky blue); all hydrogen atoms have been omitted for clarity.

It should be pointed out that the polyanion **1** somewhat resembles $[Pd_2Na_2KAs_4W_{40}O_{140}(H_2O)]^{21}$ previously reported by Ulrich Kortz and coworkers, in which two sites are occupied by two Pd atoms and two Na atoms (Figure S2a).¹⁴ Nevertheless, there are also obvious differences between them, despite containing the same As₄W₄₀ unit: a) the former consists of a tetra-Ru-containing heterometallic core $[{Ru}_4(H_2O)_4](WO_2)_4]^{20+}$, whereas the latter includes a dual-Pd-containing bimetal-oxide core $[Pd_2W_4O_8(H_2O)]^{12+}$; b) in the former, four Ru atoms are hexa-coordinated and defined by one As atom, one water molecule and four μ_2 -O atoms; on the contrary, the two Pd atoms in the latter are all four-coordinated and defined by three μ_2 -O atoms and one As atom. Similarly, the polyanion **1** somewhat resembles $[As_4W_{40}O_{140}{Ru}_2(CH_3COO)]_2]^{14-}$ previously reported by Niu and coworkers, in which two bidentate acetic acid ligands connects four Ru atoms (Figure S2b).¹⁵



Fig. S3 a) Combined polyhedral/ball-and-stick representation of polyanion for **1**. b) Combined polyhedral/ball-andstick representation of polyanion for **1-dehyd-373K**. c) Combined polyhedral/ball-and-stick representation of polyanion for **1-dehyd-473K**. d) Combined polyhedral/ball-and-stick representation of polyanion for **1-dehyd-573K**. Color code: O (red), Ru (yellow), As (pink), WO₆ octahedra (sea green) and bridging group WO₆ octahedron (sky blue); all hydrogen atoms have been omitted for clarity.



Fig. S4 a) The eight-membered metal ring $[{Ru_4(H_2O)_4}(WO_2)_4]^{20+}$ unit in **1**. b) The eight-membered heterometallic $[Ru_4(WO_2)_4]^{20+}$ core in **1-dehyd-573K**. c) Coordination environment of the Ru1 ion of **1**. d) The simplified connective mode of the $[{Ru_4(H_2O)_4}(WO_2)_4]^{20+}$ unit that displays a cage configuration. e) Coordination environment of the Ru1 ion of **1-dehyd-573K**. f) The trigonal-pyramid geometry of the tetranuclear Ru cluster.

Supplementary Physical Characterizations

Structural Descriptions and General Comments. Bulk samples of the compounds are crystalline and homogeneous to the eye, and all were characterized by elemental analysis, PXRD, IR TG and XPS spectroscopy in the Supporting Information.^{16,17} The phase purity of title compounds was certified by PXRD measurement.



Fig. S5 a) The IR spectra of 1 (black) and 1 after the removal of H_2O molecules (other color). b) The temperature dependence of IR spectra of 2.

IR spectra. Infrared spectra were collected for compounds **1** and **2** as pressed KBr disks. Comparison five vibration bands of the fingerprint region below 1000 cm⁻¹ is informative (Figure S5), as this region is dominated by the intense bands of the Keggin-type polyanion backbone. The spectra for compounds **1** and **2** are similar, with five vibration bands in the region 500–1000 cm⁻¹. Four of these broad bands between 700 and 1000 cm⁻¹ strongly resemble the spectrum of the K₁₄[As₂W₁₉O₆₇(H₂O)] precursor and are assigned as follows: the broad band at ~950 cm⁻¹ is ascribed to the terminal W–O stretch, the band at 840 cm⁻¹ with a shoulder at 880 cm⁻¹ is due to the corner-sharing W–O–W stretches, and the two bands at ~710 and ~790 cm⁻¹ are due to edge-sharing W–O–W stretches,¹⁸ possibly overlapping with

the As–O–W stretches.¹⁵ The broad peaks at ~3500 and ~1630 cm⁻¹ can be assigned to the stretching and bending modes of lattice water molecules.¹⁹ The OH stretching and OH bending bands at 3500 and 1630 cm⁻¹, respectively, are observed at room temperature. As the temperature increases, the intensity of these bands decreases (Figure S5). At 573 K, these bands almost disappear, that is, all H₂O molecules are removed from **1**.



Fig. S6 The thermogravimetric curves of 1 and 2.

Thermogravimetric Analyses. The thermal stability of **1** and **2** have been investigated under a nitrogen flow between 30 and 850 °C by thermogravimetric analysis (TGA) (Figure S6). The TGA curve exhibits two-step weight loss process. The first weight loss of 6.37% or 4.89% from 30 to 300 °C are attributed to twirty-six or twenty-nine crystalline water molecules (calc. 6.41% or 4.83%). The second weight loss corresponds to the decomposition of POM skeleton.

Determination of Solution Structure and Stability. Because the incorporation of four Ru atoms and the different dehydration degree of **1** resulted in an obvious change of solubility in water or organic solvent. It was important to test the solution stability of **1** and **2** in different solutions environments to investigate their reactive condition in a variety of catalytic reaction systems. Therefore, solution stability studies were performed on UV/Vis and ESI-MS characterization methods for the different dehydration degree of **1** and **2**. In the first instance, UV/Vis spectra of compounds provide a simple probe for monitoring changes in the degree of stability over time and pH value (Figure S7). Furthermore, ESI-MS was conducted to provide the cluster species information in solution before and after catalysis at room temperature (Figures S8–S10, S12, S13 and Tables S1–S4).

UV/Vis spectra. The UV/Vis spectra of **1** and **1-dehyd-573K** in dilute aqueous solution (1.0×10^{-6} mol/L) displays two obvious characteristic absorption bands at 196 and 246 nm in the range 400–190 nm (Figure S7). The higher energy absorption at 196 nm can be attributed to the p π -d π charge-transfer transition of the O_t \rightarrow W bonds, whereas that an inconspicuous absorption band appeared at 246 nm can be ascribed to the p π -d π charge-transfer transition of the O_{b, c} \rightarrow W bonds.²⁰ In the visible region, an inconspicuous broad peak at around 475 nm is observable in moreconcentrated solution (1.0×10^{-4} mol/L), which can be assigned to O \rightarrow Ru charge transfer.²¹ The UV spectra of **1** before and after removal of all H₂O in dilute solution are similar to each other (Figure S7). The pH-dependent absorption spectra of **1** and **1-dehyd-573K** in the visible region at a range of pH (2.0-11.0) were also investigated as POMs are known to be pH-sensitive. The self-buffering pH of **1** and **1-dehyd-573K** in aqueous solution were about 5.0. As shown in Figure S7c and S7f, as the pH was lowered, the absorption band at around 475 nm became progressively weaker. In contrast, the absorption band was gradually red-shifted at pH >

9.0. Furthermore, the influences of time-dependent on the stability of chemical mixtures have been conducted by UV absorption spectra in aqueous systems (Figure S7b and S7e). The UV spectra of both compounds remained unchanged with different aging times (0–8 h), and they were stable in the pH value ranges of 3.0–10.0 at ambient temperature (Figure S7c and S7f).



Fig. S7 UV/Vis spectra of **1**: a) in dilute solution ($1.0 \times 10^{-6} \text{ mol/L}$), b) in more concentrated solution ($1.0 \times 10^{-4} \text{ mol/L}$), and c,) at different pH values. UV/Vis spectra of **1-dehyd-573K**: d) in dilute solution ($1.0 \times 10^{-6} \text{ mol/L}$), e) in more concentrated solution ($1.0 \times 10^{-4} \text{ mol/L}$), and f,) at different pH values.



Fig. S8 a) The pH-dependent ESI-MS spectra of **1** solution after adding HCl and NaOH. b) The pH-dependent ESI-MS spectra of **2** solution after adding HCl and NaOH.

Furthermore, the influence of the pH values on structures for **1** and **2** were studied.²² The selfbuffering pH of aqueous solutions are about 4.70 and 4.90 for **1** and **2**, respectively. Addition of 1 M HCl and 1 M NaOH could lead to the disintegration of polyanions in solution. In the pH range of 2.0–10.0, the dominant peaks of intact polyanions **1** were clearly observed (Figure S8a). The peaks assignable to the clusters gradually disappeared when the pH value was reduced under 2.0 by 1 M HCl, indicating that the structure of **1** may be destroyed. The intensity of peaks of intact polyanion **1** decreases with increasing the pH value above 11.0 by 1 M NaOH, which proves the decomposition of the cluster (Figure S8a). Hence, a conclusion was drawn that the intact polyanion **1** kept steady in a broad range pH value (2.0–11.0) in aqueous solutions. However, the polyanion cluster **2** is still stable in a narrow pH value region of 3.0–7.0 (Figure S8b). When titrating with 1 M HCl or 1 M NaOH, the dominant peak intensity significantly decreases in abundance at pH < 3.0 or pH > 7.0 (Figure S8b).

1-dehyds (1-dehyd-373K, 1-dehyd-473K, 1-dehyd-573K) (5 mg) were dissolved in 10 mL of ethyl alcohol with stirring, respectively. Immediately, the light black solution was sealed in a 25 mL Teflonlined autoclave and heated at 160 °C for 72 h under autogenous pressure. After cooling to room temperature, the reaction mixture was filtered and ESI-MS measurements carried on an ABSCIEX triple-TOF 4600 mass spectrometer.



Fig. S9 1-dehyd-473K dissolved in methyl alcohol: a) ESI mass spectrum corresponding to the intact cluster at around 1503.123 and 1759.316. b) Zoom-in of the peaks at around m/z 1503.123. c) Zoom-in of the peaks at around m/z 1759.316. d) The simulated isotope pattern (red) and experimental data (black) at around m/z 1503.123.



Fig. S10 1-dehyd-573K dissolved in methyl alcohol: a) ESI mass spectrum corresponding to the intact cluster at around 1500.544 and 1754.298. b) Zoom-in of the peaks at around m/z 1500.544. c) Zoom-in of the peaks at around m/z 1754.298. d) The simulated isotope pattern (red) and experimental data (black) at around m/z 1500.544.



Fig. S11 a)The IR spectra of 1 before and after catalysis and 1-dehyd-573K after catalysis. b) The PXRD patterns of 1 before and after catalysis and 1-dehyd-573K after catalysis.



Fig. S12 After catalysis **1** dissolved in methyl alcohol: a) ESI mass spectrum corresponding to the intact cluster at around 1503.400 and 1764.298. b) Zoom-in of the peaks at around m/z 1503.400. c) Zoom-in of the peaks at around m/z 1764.298. d) The simulated isotope pattern (red) and experimental data (black) at around m/z 1764.298.



Fig. S13 After catalysis **1-dehyd-573K** dissolved in methyl alcohol: a) ESI mass spectrum corresponding to the intact cluster at around 1506.465 and 1757.563. b) Zoom-in of the peaks at around m/z 1506.465. c) Zoom-in of the peaks at around m/z 1757.563. d) The simulated isotope pattern (red) and experimental data (black) at around m/z 1506.465.



Fig. S14 XPS spectra for a) Ru 3d and b) W 4f of compound **1**. XPS spectra for c) Ru 3d and d) W 4f of compound **1dehyd-573K**. Spectra analysis was carried out using peak fitting with Gaussian–Lorentzian peak shape and Shirley type background subtraction, and the C 1s peak typically locates at 284.6 eV taking as a reference.

XPS analyses. X-ray photoelectron spectra were measured of W 4f and Ru 3d spectra for compounds **1** and **1-dehyd-573K** (Figure S14). Literature binding energies for the W $4f_{7/2}$ and $4f_{5/2}$ peaks average around 35.5 and 37.9 eV for W^{V1} and 34.1 and 36.7 eV for W^{V.23} The W 4f spectra for **1** and **1-dehyd-573K** all exhibit only the doublet associated with W^{V1} at binding energies of 35.28–35.30 and 37.43–37.46 eV, with no indication of W^V in two compounds. Literature binding energies for the Ru $3d_{5/2}$ and $3d_{3/2}$ peaks average around 281.6 and 285.8 eV for Ru^{II}, 282.0 and 286.6 eV for Ru^{III}, 282.0 and 287.2 eV for Ru^{IV}, and 285.4 and 289.1 eV for Ru^{V.24}



Fig. S15 The thermogravimetric curves of a) 1-dehyd-373K, b) 1-dehyd-473K, c) 1-dehyd-573K.



Fig. S16 Catalytic device for oxidative catalysis of 1-(4-chlorophenyl)ethanol under very mild conditions.

Charge	Observed M/z	Calculated M/z	Polyanion
-7	1503.123	1503.085	$\{NaK_{3}H_{5}As_{4}W_{40}O_{140}Ru_{4}(H_{2}O)_{4}\}^{7-}$
-6	1759.316	1759.431	$\{K_4H_6As_4W_{40}O_{140}Ru_4(H_2O)_5\}^{6-}$

Table S1. Assignment of peaks in negative mode mass spectra of 1-dehyd-473K.

Charge	Observed M/z	Calculated M/z	Polyanion
-7	1500.544	1500.498	$\{K_5H_4As_4W_{40}O_{140}Ru_4\}^{7-}$
-6	1754.298	1754.412	$\{NaK_5H_4As_4W_{40}O_{140}Ru_4\}^{6-}$

Table S2. Assignment of peaks in negative mode mass spectra of 1-dehyd-573K.

 Table S3. Assignment of peaks in negative mode mass spectra of after catalysis of 1.

Charge	Observed M/z	Calculated M/z	Polyanion
-7	1503.400	1503.550	$\{KH_8As_4W_{40}O_{140}Ru_4(H_2O)_{10}\}^{7-}$
-6	1764.298	1764.322	$\{NaK_2H_7As_4W_{40}O_{140}Ru_4(H_2O)_{10}\}^{6\cdot}$

 Table S4. Assignment of peaks in negative mode mass spectra of after catalysis of 1-dehyd-573K.

Charge	Observed M/z	Calculated M/z	Polyanion
-7	1506.321	1506.211	$\{NaK_5H_3As_4W_{40}O_{140}Ru_4(H_2O)\}^{7-1}$
-6	1757.563	1757.414	$\{NaK_5H_4As_4W_{40}O_{140}Ru_4(H_2O)\}^{6-1}$

	1	1-dehyd-373K	1-dehyd-473K	2
empirical formula	NaK ₅ H ₉₀ As ₄ Ru ₄ -	$NaK_5H_{30}As_4Ru_4$ -	KH ₁₅ As ₄ Ru ₄ -	KNa ₁₂ H ₇₅ Cl ₂ As ₄ -
	W ₄₀ O ₁₈₀	W ₄₀ O ₁₅₀	$W_{40}O_{140}$	$W_{40}O_{169}$
formula weight	11246.65	10706.20	10351.6998	10818.66
temperature (K)	150.00	298.00	296.15	298.00
crystal system	tetragonal	tetragonal	tetragonal	triclinic
space group	I-4	I-4	I-42m	P-1
<i>a</i> /Å	19.6886(13)	19.8405(12)	19.471(7)	19.178(3)
b/Å	19.6886(13)	19.8405(12)	19.471(7)	19.677(3)
<i>c</i> /Å	26.1118(19)	26.2174(17)	23.563(8)	30.803(5)
α /deg	90	90	90	94.414(5)
β/deg	90	90	90	98.453(5)
γ/deg	90	90	90	116.279(4)
V/Å ³	10122.0(15)	10320.4(14)	8933(7)	10176(3)
Ζ	2	2	2	2
$ ho_{ m calc}$ /g cm ⁻³	3.608	3.405	3.843	3.561
μ /mm⁻¹	23.757	23.284	26.800	23.319
2∂ range/deg	4.882 to 50.198	4.846 to 50.154	4.55 to 50.178	4.286 to 50.198
index ranges	–23 ≤ h ≤ 23,	–22 ≤ h ≤ 23,	–18 ≤ h ≤ 19,	–22 ≤ h ≤ 22,
	$-23 \le k \le 20,$	$-23 \le k \le 22,$	$-21 \le k \le 23,$	–23 ≤ k ≤ 23,
	-31 ≤ ≤ 31	- 31 ≤ I ≤ 31	–28 ≤ l ≤ 26	- 36 ≤ l ≤ 36,
refins collected	24650	31769	21881	111285
independent reflens	8802	9164	4160	36142
R _{int}	0.0776	0.0939	0.0951	0.0696
data/restraints/parameters	8802/42/451	9164/48/442	4160/90/240	36142/0/2039
GOF on F ²	1.048	0.991	1.046	1.010
$R_1, wR_2 [l > 2\sigma(l)]$	0.0481, 0.1141	0.0573, 0.1477	0.0841, 0.2223	0.0443, 0.0881
R_1 , wR_2 [all data]	0.0605, 0.1196	0.0712, 0.1575	0.1493, 02929	0.0722, 0.0989

 Table S5. Crystallographic Data Parameters for 1, 1-dehyd-373K, 1-dehyd-473K and 2.

Cat	Oxidant/equiv.	т	t/h	Yield %	Ref.
DPyAM(H)-PW (0.04 mmol)	H ₂ O ₂ (6.0)	90 °C	0.5	97	25
Na _{6.3} Fe _{0.9} [AlMo ₁₁ O ₃₉]·2H ₂ O (0.01 mmol)	Air (1.0 atm)	80 °C	1	96	26
[bmim] ₅ [PW ₁₁ ZnO ₃₉]·3H ₂ O (0.05 mmol)	H ₂ O ₂ (10.0)	reflux	1.25	100	27
K ₅ NaH ₁₀ [{Ru ₄ (H ₂ O) ₄ }(WO ₂) ₄ (AsW ₉ O ₃₃) ₄]·26H ₂ O	TBHP (aq.) (2.0)	25℃	2	87	This
(0.001 mmol)					work
1-dehyd-573K (0.001 mmol)	ТВНР (аq.) (2.0)	25℃	2	99	This work
LDH-PWFe (0.01 mmol)	H ₂ O ₂ (5.0)	reflux	2.5	100	28
H[Cu ₅ ¹ Cu ¹¹ (pzc) ₂ (pz) _{4.5} {P ₂ W ₁₈ O ₆₂ }]·6H ₂ O	TBHP (3.0)	60 °C	3	97	29
(0.002 mmol)					
Pd-(VO) ₄ P ₂ W ₁₈ /mAPO (0.002 mmol)	O ₂ (1 atm)	80°C	3	68	30
K ₁₁ [Pr(PW ₁₁ O ₃₉) ₂]·22H ₂ O (0.0012 mmol)	H ₂ O ₂ (2.0)	90°C	3	99	31
K ₈ [BW ₁₁ O ₃₉ H]·13H₂O (0.015 mmol)	H ₂ O ₂ (2.0)	90°C	3	98	32
H ₃ PW ₄ O ₁₂ (50 mg)	H ₂ O ₂ (4.0)	80°C	3	99	33
PWFe/SiO ₂ (0.03 mmol)	H ₂ O ₂ (10.0)	reflux	4	92	34
IL/SMNP (0.02 mmol)	O ₂ (2 atm)	80°C	5	97	35
PW/DAIL/MIL-101(Cr) (0.006 mmol)	TBHP (4.5)	100°C	6	95	36
H ₅ PV ₂ Mo ₁₂ O ₄₀ (1 mmol)	O ₂ (1 atm)	135°C	4	100	37
V ₂ ILSBA (0.0002 mmol)	Air (3.4 atm)	100°C	6	99	38
TEMPO/H ₅ PV ₂ Mo ₁₀ O ₄₀ (0.01 mmol)	O ₂ (2 atm)	100°C	6	98	39
[Pd(dpa) ₂ {VO(DMSO) ₅ } ₂][PMo ₁₂ O ₄₀] ₂ -	O ₂ (1 atm)	130°C	8	99	6
·4DMSO					
(0.00625 mmol)					
Na ₁₂ [WZnZn ₂ (H ₂ O) ₂ (ZnW ₉ O ₃₄) ₂] (5 mmol)	H ₂ O ₂ (5.0)	85°C	7	100	40
Na ₁₂ [WZnZn ₂ (H ₂ O) ₂ (ZnW ₉ O ₃₄) ₂] (0.004 mmol)	H ₂ O ₂ (5.0)	75°C	7	100	41
Ni ₇ -Ale ₂ (0.002 mmol)	H ₂ O ₂ (5.0)	85°C	7	95	42
NENU-9HP-1/120 (0.005 mmol)	TBHP (4.0)	100°C	7	97	43
Cs ₅ (V ₁₄ As ₈ O ₄₂ Cl) (0.005 mmol)	TBHP (5.0)	25°C	12	100	4
$Q_4[M(dmso)_3Mo_7O_{24}]$ (M = Ru(II), Os(II))	O ₂ (2 atm)	120°C	12	98	44
(0.01 mmol)					
[{nBu ₄ N} ₅ {PV ₂ Mo ₁₀ O ₄₀ }] (0.02 mmol)	N ₂ O (1 atm)	150°C	15	99	45

 Table S6. Comparison of reported POM-based catalysts for the oxidation of alcohols.

Table S7. Catalytic oxidation of 1-(4-chlorophenyl)ethanol with 1. ^a

entry	cat.	Reaction system	Yield ^b /%
1	blank	homogeneous	9.2
2	As_2W_{19}	homogeneous	8.5
3	RuCl₃	homogeneous	44.2
4	As ₂ W ₁₉ /RuCl ₃	homogeneous	46.2
5	2	heterogeneous	13.0
6	2/RuCl ₃	homogeneous	52.3
7	1	heterogeneous	67.87
8	1-dehyd-373K	heterogeneous	69.20
9	1-dehyd-473K	heterogeneous	72.22
10	1-dehyd-573K	heterogeneous	89.10

^{*a*} Reaction conditions: 1-(4-Chlorophenyl)ethanol (1 mmol), TBHP (aq.) (2 mmol), catalysts (0.1 mol %), solventfree, room temperature, t = 1 h. ^{*b*} GC yields and conversions for target product acetophenone were based on naphthalene as internal standard. All the products were identified by GC-MS and GC spectra.

	Yield ^b (%)						
Time (h)	1	1-dehyd-373K	1-dehyd-473K	1-dehyd-573K	2		
0.5	43.7	46.5	48.5	76.5	10.8		
1.0	67.9	69.2	72.2	89.1	13		
1.5	79.3	80.9	83.6	95.8	13.9		
2.0	86.8	88.4	90.3	98.5	15.5		
2.5	92.7	94.5	95.6	99.6	17.2		
3.0	95.9	96.9	97.3	99.8	19.3		
3.5	97.7	98.6	98.9	99.9	20.9		
4.0	98.6	98.9	99.2	99.9	22.1		

Table S8. The rates of catalytic reaction for 1, 1-dehyd-373K, 1-dehyd-473K, 1-dehyd-573K and 2.^a

^{*a*} Reaction conditions: 1-(4-Chlorophenyl)ethanol (1 mmol), TBHP (aq.) (2 mmol), catalyst (0.1 mol %), solvent-free, room temperature. ^{*b*} GC yields and conversions for target product acetophenone were based on naphthalene as internal standard. All the products were identified by GC-MS and GC spectra.

Time (h)	Catalyst dose/Yield ^b (%)				
	0.1 mol %	0.05 mol %	0.025 mol %	0.0125 mol %	0 mol %
0.5	43.7	31.1	17.4	10.3	8.5
1.0	67.9	50.2	30.9	15.4	9.2
1.5	79.3	65.3	41.4	19.3	9.5
2.0	86.8	75.4	50.3	23.4	9.6
2.5	92.7	83.2	58.8	26.1	9.9
3.0	95.9	89.3	66.0	28.7	10.5
3.5	97.7	94.5	70.5	30.5	11.0
4.0	98.6	97.8	73.8	31.4	11.4
TON	986	1956	2952	2512	
TOF	246.5 h ⁻¹	489 h ⁻¹	738 h ⁻¹	628 h ⁻¹	

Table S9. The rates of catalytic reaction with different molar amount of 1. ^a

^{*a*} Reaction conditions: 1-(4-Chlorophenyl)ethanol (1 mmol), TBHP (aq.) (2 mmol), solvent-free, room temperature. ^{*b*} GC yields and conversions for target product acetophenone were based on naphthalene as internal standard. All the products were identified by GC-MS and GC spectra.

Table S10. The rates of catalytic reaction with different molar amount of 1-dehyd-573K. ^a					
ïme (h)	Catalyst dose/Yield ^b (%)				
	0.1 mol %	0.05 mol %	0.025 mol %	0.0125 mol %	0 mal

1

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Time (n)					
	0.1 mol %	0.05 mol %	0.025 mol %	0.0125 mol %	0 mol %
0.5	76.5	66.0	42.6	18.7	8.5
1.0	89.1	80.2	60.0	30.3	9.2
1.5	95.8	87.3	67.5	39.5	9.5
2.0	98.5	93.1	76.3	46.7	9.6
2.5	99.6	96.5	81.1	51.2	9.9
3.0	99.8	97.8	83.8	55.8	10.5
3.5	99.9	98.7	85.4	58.3	11.0
4.0	99.9	99.1	86.5	60.0	11.4
TON	999	1982	3460	4800	
TOF	249.75 h ⁻¹	495.5 h ⁻¹	865 h ⁻¹	1200 h ⁻¹	

^{*a*} Reaction conditions: 1-(4-Chlorophenyl)ethanol (1 mmol), TBHP (aq.) (2 mmol), solvent-free, room temperature. ^{*b*} GC yields and conversions for target product acetophenone were based on naphthalene as internal standard. All the products were identified by GC-MS and GC spectra.

Table S11. The rates of catalytic reaction for the large-scale experiment of 1. ^a

Time (h)	Large-scale experiment/Yield ^b (%)			
	Five times	Ten times	Five times of blank	Ten times of blank
0.1	28.8	15.4	15.3	13.6
0.5	44.1	20.3	17.6	15.3
1.0	57.6	24.4	19.7	17.3
1.5	64.4	28.9	21.8	19.3
2.0	70.2	32.4	22.7	19.7
2.5	74.6	35.4	23.7	20.2
3.0	78.9	38.0	24.8	20.5
3.5	82.7	40.5	25.5	20.7
4.0	84.3	41.3	26.3	20.7
TON _{initial}	1440	1540		
TOF _{initial}	14400 h ⁻¹	15400 h ⁻¹		
TON _{final}	4215	4130		
TOF _{final}	1053.75 h ⁻¹	1032.5 h ⁻¹		

^{*a*} Reaction conditions: 1-(4-chlorophenyl)ethanol (5/10 mmol), TBHP (aq.) (10/20 mmol), catalyst (0.1 mol %), solvent-free, room temperature. ^{*b*} GC yields and conversions for target product acetophenone were based on naphthalene as internal standard. All the products were identified by GC-MS and GC spectra.

	Large-scale experiment/Yield ^b (%)			
Time (h)	Fifteen times	Twenty times	Fifteen times of blank	Twenty times of blank
0.1	25.1	20.3	14.4	13.3
0.5	40.9	28.9	17.6	16.1
1.0	57.9	39.7	19.7	17.6
1.5	69.0	49.7	20.8	18.2
2.0	78.3	58.3	20.7	18.5
2.5	85.6	64.8	20.9	18.3
3.0	90.6	68.2	21.0	18.6
3.5	94.1	70.7	21.0	18.7
4.0	96.8	71.6	21.3	18.8
TON _{initial}	2510	4060		
TOF _{initial}	25100 h ⁻¹	40600 h ⁻¹		
TON _{final}	14520	14320		
TOF _{final}	3630 h ⁻¹	3580 h ⁻¹		

Table S12. The rates of catalytic reaction for the large-scale experiment of 1-dehyd-573K. a

^{*a*} Reaction conditions: 1-(4-chlorophenyl)ethanol (15/20 mmol), TBHP (aq.) (30/40 mmol), catalyst (0.1 mol %), solvent-free, room temperature. ^{*b*} GC yields and conversions for target product acetophenone were based on naphthalene as internal standard. All the products were identified by GC-MS and GC spectra.

Table S13. Optimization of the different reaction conditions for the catalytic oxidation of 1-(4chlorophenyl)ethanol with 1^{-g}

entry	cat./mol %	TBHP (aq)/equiv	Yield ^b /%		
1	0.05	2	37.3		
2	0.1	2	86.8		
3	0.15	2	80.9		
4	0.1	1	53.5		
5	0.1	0	25.6		

^{*a*} Reaction conditions: 1-(4-Chlorophenyl)ethanol (1 mmol), solvent-free, room temperature, t = 2 h. ^{*b*} GC yields for target product were based on methylbenzene as internal standard. All the products were identified by GC-MS and GC spectra.

Table S14. BVS values of Ru, As, W and selected O atoms of compound 1.

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
Ru1	2.905	As1	2.425	W1	5.844	W2	6.498
W3	6.242	W4	6.001	W5	6.088	W6	6.436
W7	5.871	W8	5.593	W9	6.190	W10	6.330
01	0.349	02	1.410	03	1.703	04	2.070
05	2.160	06	2.155	07	1.858	08	1.488
09	1.918	010	2.146	011	1.984	012	1.858
013	1.919	014	1.750	015	1.703	016	2.009
017	1.947	018	1.934	019	1.822	O20	2.033
021	2.019	022	1.529	023	2.011	024	1.448
025	1.798	025	2.071	027	2.167	028	1.840
029	1.726	O30	2.001	031	1.987	032	2.043
033	1.937	O34	1.658	O35	1.890	O36	2.082

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
Ru1	3.646	As1	3.294	W1	5.974	W2	6.595
W3	5.438	W4	5.857	W5	6.396	W6	6.781
W7	5.910	W8	6.430	W9	5.817	W10	6.358
01	0.501	02	2.057	03	2.123	04	1.942
05	2.113	06	1.964	07	1.452	08	2.133
09	1.860	O10	1.813	011	1.847	012	1.959
013	2.122	014	2.127	015	1.613	016	1.376
017	1.958	018	2.147	019	1.739	O20	2.002
021	1.982	022	2.016	023	1.868	O24	1.949
025	1.931	O26	1.929	027	1.529	O28	2.108
O29	1.570	O30	1.887	O31	1.998	O32	1.779
O33	2.172	O34	1.924	O35	2.075	O36	1.372

 Table S15. BVS values of Ru, As, W and selected O atoms of compound 1-dehyd-373K.

Table S16. BVS values of As, W and selected O atoms of compound 2.

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
As1	3.042	As2	2.900	As3	2.956	As4	3.077
W1	6.150	W2	6.181	W3	6.148	W4	6.092
W5	6.095	W6	6.043	W7	6.222	W8	6.045
W9	6.021	W10	6.187	W11	6.125	W12	5.941
W13	6.135	W14	6.070	W15	6.086	W16	5.983
W17	6.061	W18	6.246	W19	6.343	W20	6.139
W21	6.028	W22	6.140	W23	6.046	W24	6.185
W25	6.000	W26	6.003	W27	6.005	W28	6.363
W29	6.240	W30	6.050	W31	6.142	W32	6.040
W33	6.062	W34	6.077	W35	6.023	W36	6.161
W37	6.114	W38	6.084	W39	6.044	W40	6.101
O68	1.963	O69	1.931	070	1.698	071	1.929
072	1.943	073	1.939	074	1.855	075	1.653
076	1.764	077	2.005	078	1.584	079	1.817
O80	1.808	081	1.918	082	1.869	083	1.579
084	1.905	O85	1.570	O86	1.533	087	1.609
O89	2.004	O90	1.680	O91	1.864	O92	2.105
093	1.662	094	2.046	O 95	1.676	O96	1.902
097	2.027	O98	2.054	O99	1.788	O100	1.935
O101	1.783	O102	1.930	O103	1.966	0135	1.635

Table S17. Effect of radical trap on the oxidation of 1-(4-chlorophenyl)ethanol with 1. a

entry	Radical trap	mmol	Yield ^b /%
1	-	-	86.8
2	Ph₂NH	0.125	6.8
3	Ph ₂ NH	0.250	6.6
4	Ph ₂ NH	0.500	2.1
5	TEMPO	0.125	65.3
6	TEMPO	0.250	62.3
7	TEMPO	0.500	54.4

^{*a*} Reaction conditions: 1-(4-Chlorophenyl)ethanol (1 mmol), TBHP (aq.) (2 mmol), catalyst (0.1 mol %), solvent-free, room temperature, t = 2 h. ^{*b*} GC yields and conversions for target product acetophenone were based on naphthalene as internal standard. All the products were identified by GC-MS and GC spectra.

Table S18. Reusability of catalysts 1 and 1-dehyd-573K in the catalytic oxidation of 1-(4-chlorophenyl)ethanol. a

Use	Yield ^b /%	Yield ^b /%
1st	86.8	98.5
2nd	86	97.9
3rd	85.3	97.6
4th	84.1	96.2
5th	83	95
6th	82.4	94.5

^{*a*} Reaction conditions: 1-(4-Chlorophenyl)ethanol (1 mmol), TBHP (aq.) (2 mmol), solvent-free, room temperature, t = 4 h. ^{*b*} GC yields for target product were based on methylbenzene as internal standard. All the products were identified by GC-MS and GC spectra.

Table S19. The catalytic oxidation of 1-(4-chlorophenyl)ethanol with 1 and 1-dehyd-573K. a

entry	cat./mol %	t/h	Yield ^b /%	Selectivity/%
1	0.1 (1)	2	86.8	>99
2	0.1 (1)	4	98.6	>99
3	0.1 (1)	6	98.9	>99
4	0.1 (1)	8	99.5	>99
5	0.1 (1-dehyd-573K)	2	98.5	>99
6	0.1 (1-dehyd-573K)	4	99.9	>99
7	0.1 (1-dehyd-573K)	6	99.9	>99
8	0.1 (1-dehyd-573K)	8	99.9	>99

^{*a*} Reaction conditions: 1-(4-Chlorophenyl)ethanol (1 mmol), TBHP (aq.) (2 mmol), solvent-free, room temperature. ^{*b*} GC yields for target product were based on methylbenzene as internal standard. All the products were identified by GC-MS and GC spectra.

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